[illegible] cell	Enzyme	Substrate	Product
[illegible]ast cell	Zymase	Dextrose	$CO_2 + C_2H_5OH$
[illegible]ivary cell	Ptyalin	Boiled Starch.	Dextrin Maltose.

Allotropy is that condition in which ~~[illegible]~~ an ~~diff~~ element may exist in 2 or more diff modification.

To clear solution add Ba Cl + the ~~[illegible]~~ white ~~[illegible]~~ down sulphur or sulphuric acid insol. in H

To sulphite add Ba Cl a white ppt sol in HCl.

sulphide add HCl and odor of H_2S is given off turns filter paper wet in lead acet black

M. de Larkin

167

Larkin

Fermentation refers to bubbling.

Fermentation is a ~~slight~~ cyclic chemical change taking place in a chem. system by means of a ... at the end of the cycle the chem system is permanently altered but the ferment remains unchanged.

Ferment is an active chemical substance capable of producing a cyclic chemical change in a chemical system at end of cycle the chemical system permanently altered but the ferment is unchanged

Enzyme is a ferment which contains carbon results from metabolism

Ba Sr Ca not CO_3 phosphor

DR. JOSEPH S. SCHMUCKLER
Prof. Chemistry & Science Educ.
452 Ritter Hall, Temple University
Philadelphia, PA 19122 USA

alcohol burns with a non
luminous flame which does no
deposit soot.
odor and taste

Martin J. Larkin

ELEMENTS OF GENERAL CHEMISTRY

LONG

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ELEMENTS

OF

GENERAL CHEMISTRY

WITH

EXPERIMENTS

BY

JOHN H. LONG, M.S., Sc.D.

PROFESSOR OF CHEMISTRY AND DIRECTOR OF THE CHEMICAL LABORATORIES IN THE NORTHWESTERN UNIVERSITY MEDICAL SCHOOL

FOURTH EDITION—REVISED AND ENLARGED

Illustrated

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PREFACE TO THE FOURTH EDITION.

In the preparation of this revision some additions have been made in the presentation of chemical theory and in the description of new substances. Most of the added matter is given in a chapter, not in the older editions, on the theories of solution and the conditions of chemical equilibrium. These topics are treated in an elementary manner suited to the needs of Freshmen students, but while the discussion is necessarily brief it is considered sufficient for this stage of a college course.

To my wife, Catherine Stoneman Long, I am greatly indebted for the preparation of the index, and to my colleague, Dr. Walter H. Buhlig, for valuable assistance in the reading of the proofs.

THE AUTHOR.

CHICAGO, June, 1906.

ELECTROLYTIC DETERMINATIONS AND SEPARATIONS

THESIS

Presented to the Faculty of the Department of Philosophy of the University of Pennsylvania,
For the Degree of Doctor of Philosophy

BY

LILY GAVIT KOLLOCK, A. B.

PHILADELPHIA, PA.

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INTRODUCTION.

That the electric current has greatly aided in the development of new and reliable methods for the determination and separation of metals is no longer questioned. That new material will continue to be added to what we now possess is also certain to occur. But in the old methods, worked out long before correct ideas prevailed as to current density, concentration of the solution and electrode surface, gaps exist, and uncertainty must necessarily prevail in the minds of those who seek to reproduce the proper working conditions of these earlier methods. That the latter are in every sense satisfactory in the hands of those persons who are thoroughly acquainted with them is also beyond question. To render them, however, universally acceptable, and to render their place in analytical chemistry by electrolysis permanent, the absolute conditions for successful work on the part of any investigator, must be definitely established. To this end a number of the earlier methods in which the double cyanides were used as electrolytes have been carefully reviewed in the following pages, and the conditions of current density, amperage, voltage and other factors fully worked out. Thus edited, doubt can no longer be thrown upon the methods proposed, and they will continue to be in their developed condition the most reliable for the purposes for which they have been suggested. They now for accuracy, neatness and rapidity of execution most certainly excel the ordinary gravimetric and volumetric methods applied to the same metals.

It is a pleasure to acknowledge my indebtedness to Professor Edgar F. Smith, at whose suggestion this work was undertaken, and to thank him for his advice, encouragement and kindly interest.

CADMIUM.

In 1878 Smith showed that cadmium could be precipitated quantitatively from its alkaline double cyanide solution. In the following experiments cadmium sulphate containing .1659 gram of cadmium in 10 c. c. was converted into the double cyanide, using, gram of potassium cyanide. The solution was electrolyzed with a current N. $D_{100} = 0.04 - 0.06$ A and V = 2.9–3.2. The solution was heated to 60° C. After the current had passed for six hours, the deposit was washed with hot water and alcohol, dried and then weighed. The solution poured out of the platinum dish, and examined qualitatively for cadmium, showed that all the cadmium had been deposited in this time. It was likewise entirely precipitated when the current was allowed to act on the solution through the night in the cold. The following results were obtained:

RESULTS.

Cadmium.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Metal Found.
gram.	gram.						gram.
0.1659	1	125 c.c.	N. D_{100}=0.06 A.	2.9	57°	7 hours	0.1657
0.1659	1	125 c.c.	N. D_{100}=0.04 A.	2.9	cold	during night	0.1650
0.1659	1	125 c.c.	N. D_{100}=0.06 A.	3.2	60°	3 hours	0.1655

SILVER.

On page 77 of Smith's "Electro-Chemical Analysis" it is stated that silver may be precipitated from a cyanide solution containing an excess of potassium cyanide. It may be deposited with a low current, and has the advantage of non-precipitation of silver peroxide at the anode.

Accordingly a silver nitrate solution containing .1270 gram of silver in 25 c. c., after the addition of 0.5 gram of potassium cyanide, was diluted to 125 c. c. This solution was electrolyzed with a current N. $D_{100} = 0.07$ A and V = 3.2. The temperature was 65° C. The deposition was complete in three hours. With a current of N. $D_{100} = 0.1$ A the silver was deposited completely in two hours. The

relation between the current and the time factor may be seen in the following table:

RESULTS.

Silver present.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Found.
gram.	gram.					hours.	gram.
0.1270	0.5	100 c.c.	N. D_{100}=0.07 A.	3.2	65°	3	0.1271
0.1270	0.5	100 c.c.	N. D_{100}=0.07 A.	3.2	65°	3	0.1270
0.1270	0.5	100 c.c.	N. D_{100}=0.06 A.	3.2	65°	3	0.1273
0.1270	1	100 c.c.	N. D_{100}=0.01 A.	3	65°	2	0.1268
0.1026	1	100 c.c.	N. D_{100}=0 04 A.	2.5	65°	5	0.1026
0.1026	1	100 c.c.	N. D_{100}=0.04 A.	2.5	65°	5	0.1024

Separations.

SILVER FROM PLATINUM.

In the *American Chemical Journal*, volume xiii, page 417, Smith described this separation. A current of 1 c. c. of oxy-hydrogen gas per minute acted upon a solution of the double cyanide produced by adding 2.5 grams of potassium cyanide. The silver was deposited free from any trace of platinum.

The separation, therefore, was taken up in order to get the exact working conditions. The salts of the metals used were silver nitrate containing .1026 gram of silver, and platinic chloride containing from .0879 gram to .1758 gram of platinum. To the combined solutions 1.25 grams of potassium cyanide were added and the whole diluted to 125 c. c. The current used was N. $D_{100} = 0.04$ A and $V = 2.5$. The temperature was 70°. In from three to four hours the current was interrupted and the deposit washed with hot water and alcohol. It was found to be free from platinum. The filtrate gave no reaction for silver.

RESULTS.

Silver.	Platinum.	Potassium Cyanide.	Current.	Voltage.	Temperature.	Dilution.	Time.	Found.
gram.	gram.	gram.					hours.	gram.
0.1026	0.879	0.5	N. D_{100}=0.05 A.	2.5	78°	125 c.c.	5	0.1030
0.1026	0.1758	1.25	N. D_{100}=0.05 A.	2.5	75°	125 c.c.	3	0.1022
0.1026	0.1758	1.25	N. D_{100}=0.45 A.	2.4	75°	125 c.c.	3	0.1028
0.1026	0.1758	1.25	N. D_{100}=0.04 A.	2.5	75°	125 c.c.	3	0 1025
0.1026	0.1758	1.25	N. D_{100}=0.04 A.	2.5	75°	125 c.c.	3	0.1025

Silver from Copper.

In the *American Chemical Journal*, volume xi, page 264, there appears a series of forty experiments relating to the separation of these metals. Copper was found to have been precipitated with the silver when the deposition took place from a cyanide solution. It was then thought that copper could not be separated from silver by this method. In 1889 a set of new experiments was reported. By lowering the strength of the current the separation was made. The silver deposit contained no copper nor could silver be detected in the copper solution poured from the dish. In 1895 Smith and Wallace published a report of the separation made in that year.

I found that the following conditions gave accurate results. The solution of silver nitrate used contained .1024 gram of metal and that of copper nitrate contained .0998 gram of copper. To the mixed solution 2 grams of potassium cyanide were added. The liquid containing an excess of potassium cyanide was diluted to 125 c. c. This was subjected to a current of N. $D_{100} = 0.03–0.05$ A and V = 1.1–1.66. The current acted from three to seven hours. The deposit of silver was free from copper.

The results varied from the theoretical by .0002–.0003 gram.

Results.

Silver.	Copper.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Found.
gram.	gram.	grams.					hours.	gram.
0.1024	0.0998	2	125 c.c.	N. D_{100}= 0.03 A.	1.16	cold	10	0.1027
0.1024	0.1	2	125 c.c.	N. D_{100}= 0.05 A.	1.1	65°	7	0.1027
0.1024	0.1	1	125 c.c.	N. D_{100}=0.058 A.	1.66	65°	3	0.1026

Silver from Cadmium.

Smith and Spencer (*Journal of American Chemical Society*, Vol. xvi, page 420) found that the deposition of silver

was accelerated by heating the solution during the electrolysis, and that while cadmium may be entirely precipitated in the cold by the current, yet with a low current and a temperature of 60° the cadmium is held in solution. A separation of silver and mercury may be thus effected in a cyanide solution. In the same journal, Smith and Frankel record the separation of mercury from cadmium, zinc, nickel and cobalt. In 1895 Smith and Wallace published later results with the same method. Following the data thus obtained, a solution of silver nitrate containing .1024 gram of silver and cadmium sulphate solution equivalent to .168 gram of cadmium was used. The salts were transformed into their double cyanides by an excess of potassium cyanide. The silver was obtained free from cadmium in four hours. The current used was N. $D_{100} = 0.02$ A and V = 2.15. The temperature was 60° before the current was passed through the solution.

RESULTS.

Silver.	Cadmium.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Found.
gram.	gram.	grams.					hours.	gram.
0.1024	0.168	2	125 c.c.	N. D_{100}=0.02 A.	2.15	75°	4	0.1025
0.1024	0.168	2	125 c.c.	N. D_{100}=0.02 A.	2.1	60°	4	0.1020
0.1024	0.168	2	125 c.c.	N. D_{100}=0.025 A.	2.15	65°	5	0.1027

The silver in all cases was found free from cadmium.

SILVER FROM ZINC.

These metals were separated according to the following conditions: Using zinc sulphate containing .1 gram of zinc and silver nitrate solution containing .1024 gram of silver. The potassium cyanide used amounted to one gram. The solution was 125 c. c. in volume. It was electrolyzed at 70° by a current of N D_{100} = .032–.038 A and V = 2.76. In three hours the deposition of the silver was complete.

Results.

Silver.	Zinc.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Found.
gram.	gram.	gram.					hours.	gram.
0.1024	0.1	1	100 c.c.	$N.D_{100}$=0.33 A.	2.76	60°	3	0.1026
0.1024	0.1	1	100 c.c.	$N.D_{100}$=0.38 A.	2.73	70°	3	0.1028
0.1024	0.1	1	100 c.c.	$N.D_{100}$=0.38 A.	2.70	65°	3	0.1027

Nickel and cobalt were separated from silver in a similar way.

Silver from Nickel.

A solution of nickel nitrate containing .1 gram of nickel was added to a silver nitrate solution and both converted into the double cyanides by 1.5 grams of potassium cyanide. The solution was electrolyzed with a current $N. D_{100} = 0.02 - 0.03$ A and $V = 1.7 - 2$ for three hours. The separation in this time was found to be complete. The results show a variation from the calculated amount of + .0001 gram to — .0002 gram. The solution of silver in nitric acid, when examined qualitatively, gave no evidence of the presence of nickel. The nickel solution, when examined, showed that the silver had been entirely precipitated.

Results.

Silver.	Nickel.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Found.
gram.	gram.	gram.					hours.	gram.
0.1024	0.1	1.5	125 c.c.	$N.D_{100}$=0.02 A.	1.7	65°	3	0.1026
0.1024	0.1	1.5	125 c.c.	$N.D_{100}$=0.03 A.	2.	65°	5	0.1025
0.1024	0.1	1.5	125 c.c.	$N.D_{100}$=0.03 A.	1.66	60°	3	0.1025

Silver from Cobalt.

Cobalt nitrate was the salt used in this separation. To the solution of silver nitrate (.1024 gram if silver) was added a solution of the cobalt salt containing .1 gram of cobalt and 2.75 grams of potassium cyanide. A current of $N. D._{100} = 0.02$ A and $V = 2.2 - 2.7$ at a temperature of 65° was passed through the solution for five hours. The silver in this time was entirely precipitated. No cobalt was found deposited with the silver.

Results.

Silver.	Cobalt.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Found.
gram.	gram.	grams.					hours.	gram.
0.1024	0.1	2.75	125 c.c.	$N.D_{100}$=0.038 A.	2.2	65°	5	0.1028
0.1024	0.1	3.5	125 c.c.	$N.D_{100}$=0.02 A.	2.2	65°	3½	0.1027

Silver from Iron.

Heretofore these metals have not been separated electrolytically in cyanide solution. A solution of ferrous ammonium sulphate, equivalent to 0.1 gram of metallic iron, was treated with sulphurous acid in order to reduce any ferric iron which might exist. After the reduction was complete the excess of acid was nearly neutralized with potassium carbonate. To this 2.5 grams of potassium cyanide were added. The solution of the double cyanide, dark green in color, was added to a solution of silver which had been converted into the double cyanide by 0.5 gram of potassium cyanide. The entire solution was made up to 100 c. c. It was heated to 65° and electrolyzed with a current of $N. D_{100} = 0.04$ A and $V = 2.7$. At the expiration of three hours the silver was found to be entirely deposited. There was in some cases a separation of ferric oxide at the anode. The silver, after its solution in nitric acid, was tested for iron by ammonium sulphocyanide. A faint pink color, due to a trace of iron in the acid used for the solution of the metal, was observed. The deposit, which was light gray in color, varied but slightly from the theoretical amount of the silver present in the solution.

Results.

Silver.	Iron.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Found.
gram.	gram.	grams.					hours.	gram.
0.1002	0.1	3	125 c.c.	$N.D_{100}$=0.025 A.	1.8	65°	4	0.1001
0.1002	0.1	2.5	125 c.c.	$N.D_{100}$=0.02 A.	1.8	70°	4	0.1005
0.1002	0.1	3.25	125 c.c.	$N.D_{100}$=0.038 A.	2.2	65°	3	0.1000
0.1174	0.1	3	125 c.c.	$N.D_{100}$=0.04 A.	2.25	70°	3	0.1176
0.1174	0.2	4	125 c.c.	$N.D_{100}$=0.04 A.	2.2	70°	3	0.1174
0.1174	0.1	3	125 c.c.	$N.D_{100}$=0.05 A.	2.2	75°	3	0.1175

MERCURY.

In the *American Chemical Journal*, volume xi, page 264, it is recorded that mercury may be separated without difficulty with a low current and a large excess of alkaline cyanide. The deposits are noted as "compact, rather gray in color, and showed in a few cases a drop-like nature so characteristic of mercury." The time required for the deposition under the conditions given was 12–14 hours. Smith and Wallace, in the *Journal of the American Chemical Society*, in 1895, published a number of separations of mercury from other metals—zinc, cadmium, cobalt and nickel. The time required for the separation was reduced to 3 and 3½ hours.

In the experiments made this year the following conditions gave good results and confirmed those previously made. A solution of mercuric chloride, containing .1439 gram of mercury in 10 c. c. and 0.5 gram of potassium cyanide, was diluted to 100 c. c. It was electrolyzed with a current N. $D_{100} = 0.07$ A and V = 3.2. The temperature of the solution was 65° C. In three hours the metal was completely deposited. The deposit was washed with slightly warm water.

RESULTS.

Mercury.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Merc'y Found.
gram.	gram.					hours.	gram.
0.1439	0.5	100 c.c.	N. D_{100}=0.07 A.	3.2	65°	3½	0.1441
0.1439	0.5	100 c.c.	N. D_{100}=0.07 A.	3.2	65°	3½	0.1442
0.1439	0.5	100 c.c.	N. D_{100}=0.02 A.	1.6	65°	6	0.1440
0.1439	0.5	100 c.c.	N. D_{100}=0.07 A.	3.1	65°	3	0.1436

The deposits obtained were light gray in color and were easily washed. They were bright and metallic in appearance, with higher voltage.

Separations.

MERCURY FROM COPPER.

In the *American Chemical Journal*, volume xi, page 264, Smith and Frankel report the separation of mercury and

copper in an alkaline cyanide solution. A current generating 2 c. c. of oxyhydrogen gas per minute was used for this purpose. The solution used contained .1833 gram of mercury and 14–70 per cent of copper were added. With a current generating 3.2 c. c. of oxyhydrogen gas, mercury was completely deposited in sixteen hours. It is stated, however, that when the quantity of copper present exceeded 20 per cent the results were unsatisfactory. Later Smith and McCauly took up the separation again and by careful regulation of the current, were enabled to effect it even when the metals were present in equal quantities.

In repeating this work a solution of mercuric chloride equivalent to .1216 gram of mercury and a copper sulphate solution equivalent to 0.1 gram of copper were used. An excess of potassium cyanide was added. The entire solution was diluted to 125 c. c. The current acting upon the solution was N. $D_{100} = 0.04$ A and $V = 1.09$. The temperature was 65°. In from two to four hours the mercury was completely deposited. On testing the metal qualitatively, the deposit was found free from copper.

RESULTS.

Mercury.	Copper.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Merc'y Found.
gram.	gram.	grams.					hours.	gram.
0.1216	0.1	2.0	125 c. c.	N. D_{100}=0.02 A.	1.09	cold	16	0.1220
0.1216	0.1	2.5	125 c. c.	N. D_{100}=0.03 A.	1.9	65°	4	0.1216
0.1216	0.15	3.5	125 c. c.	N. D_{100}=0.035 A.	1.8	65°	2½	0.1213
0.1216	0.1	3.0	125 c. c.	N. D_{100}=0.04 A.	1.9	65°	3	0.1215

MERCURY FROM NICKEL.

These metals were separated in an analagous manner to that described under the separation of silver from nickel. To the solutions of mercuric chloride and nickel nitrate were added 2 grams of potassium cyanide. This was then diluted to 125 c. c. A current of N. $D_{100} = 0.04$ A and $V = 2.2$ was allowed to act for three hours. The deposit was found to weigh .0003 gram less than the calculated

amount of mercury present. The filtrate was found to contain no mercury. No nickel was deposited with the metal.

RESULTS.

Mercury.	Nickel.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Merc'y Found.
gram.	gram.	grams.					hours.	gram.
0.1216	0.1	2	125 c. c.	$N.D_{100}=0.04$ A.	1.7	65°	4	0.1220
0.1216	0.1	2	125 c. c.	$N.D_{100}=0.04$ A.	2.2	65°	4	0.1220
0.1216	0.15	2.5	125 c. c.	$N.D_{100}=0.04$ A.	2.2	65°	4	0.1211
0.1216	1	2	125 c. c.	$N.D_{100}=0.04$ A.	2.2	65°	4	0.1213

MERCURY FROM COBALT.

The mercuric chloride used in this separation contained .1216 gram of mercury and the cobalt nitrate contained 0.1 gram of cobalt. Two grams of potassium cyanide were added to the mixed solutions which were diluted to 100 c. c. The current acting was $N. D_{100} = 0.03$ A and $V = 2.9$. With a temperature of 60° the deposition of the mercury was complete in five hours. It was free from cobalt.

RESULTS.

Mercury.	Cobalt.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Merc'y Deposited.
gram.	gram.	grams.					hours.	gram.
0.1216	0.1	2	100 c.c.	$N.D_{100}=0.025$ A.	2.45	cold	16	0.1217
0.1216	0.1	2	100 c.c.	$N.D_{100}=0.025$ A.	2.06	65°	5	0.1213
0.1158	0.1	2	100 c.c.	$N.D_{100}=0.03$ A.	2.9	65°	5	0.1152

MERCURY FROM ZINC.

The results obtained in the separation of mercury from zinc were first reported by Smith and Frankel in 1889. The electrolysis took place at the ordinary temperature in sixteen hours, with a current generating 3 c. c. of oxyhydrogen gas per minute.

In the experiments made this year the following conditions gave satisfactory results.

RESULTS.

Mercury.	Zinc.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Found.
gram.	gram.	grams.					hours.	gram.
0.1158	0.1	2	125 c.c.	$N.D_{100}$=0.05 A.	3	60°	4	0.1152
0.1158	0.1	1.5	125 c.c.	$N.D_{100}$=0.033 A.	2.5	50°	4	0 1155
0.1158	0.2	2	125 c.c.	$N.D_{100}$=0.025 A.	2.9	50°	4	0.1155

In the third determination the current acted for three hours at 50° and then all night in the cold. The deposit in all cases was gray and compact. The mercury on examination for zinc gave no reaction for that metal, while no mercury was found in the zinc solution.

MERCURY FROM CADMIUM.

As stated under the separation of silver from cadmium, Smith and Wallace (*Journal of American Chemical Society*, 1895) found that cadmium might be separated from both silver and mercury by keeping the temperature slightly elevated. Unless this precaution is taken cadmium is precipitated with both metals, even when a low current is used.

The following proved to be good working conditions: The mercuric chloride solution used contained .1182 gram of mercury, and the cadmium sulphate solution was equivalent to .2206 gram of cadmium. The double alkaline cyanides were produced by the addition of 2.5 grams of potassium cyanide. A current of $N.D_{100} = .018$ A and $V = 1.7$ was passed through the solution, previously heated to 65° for seven hours. The mercury deposit was free from cadmium and weighed .1181 gram, which was .0001 gram lighter than the theoretical amount of mercury. It was repeatedly found that when the current was greater than 0.02 A, cadmium was precipitated.

MERCURY FROM PLATINUM.

This separation was first carried out and reported by Smith in the *American Chemical Journal*, volume xiii, p. 417.

The deposit of mercury was effected by using a current generating 2 c. c. of oxyhydrogen gas a minute. The alkaline cyanide used for .1902 gram of mercury was 2.5 grams. According to these suggestions a separation of the two metals was made. The mercury in solution was .1373 gram, and the platinum in the platinic chloride contained from .025 gram to 0.1 gram. In four hours the separation was completed. The current was N. $D_{100} = 0.05$ A and V = 2.1 to 2.3. The results show an error of—.0001 gram to + .0003 gram.

RESULTS.

Mercury.	Platinum.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Merc'y Deposited.
gram.	gram.	grams.					hours.	gram.
0.1373	0.025	3	125 c. c.	N. D_{100}=0.05 A.	2.12	65°	4	0.1372
0.1373	0.01	3	125 c. c.	N. D_{100}=0.04 A.	2.12	75°	4	0.1376
0.1373	0.01	3	125 c. 3.	N. D_{100}=0.045 A.	2.12	70°	4	0.1375

MERCURY FROM IRON.

The separation of mercury from iron, like that of silver from iron, has not been previously attempted in alkaline cyanide solution. Accordingly the following method was developed and found to yield satisfactory results:

The solution of the cyanide of iron was prepared from ferrous ammonium sulphate in precisely the same way as that described in the separation of silver from iron. The mercuric chloride solution contained .1216 gram of mercury. The cyanide present was from 1 gram to 3 grams, and the current was N. $D_{100} = 0.05$ A and V = 2.5. The temperature during the electrolysis was maintained at 70° C. In three hours the mercury was completely deposited. It was free from iron. The mercury deposit was dissolved in concentrated nitric acid. After diluting a few crystals of ammonium sulphocyanide were added. A faint pink color was observed, which was found to be due to the small trace of iron in the nitric acid.

RESULTS.

Mercury.	Iron.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Merc'y Deposited.
gram.	grams.	grams					hours.	gram.
0.1216	0.1	1	100 c.c.	$ND._{100}$=0.05 A.	2.	70°	3	0.1215
0.1216	0.3	3	100 c.c.	$ND._{100}$=0.04 A.	2.	70°	4	0.1217
0.1216	2.5	2.5	100 c.c.	$ND._{100}$=0.02 A.	2.7	65°	4	0.1217

GOLD SEPARATIONS.

In the *American Chemical Journal*, volume xiii, Smith and Muhr report the separation of gold from palladium, platinum, zinc, cobalt, nickel and copper.

GOLD FROM PALLADIUM.

It has been previously shown that palladium is not deposited with a current of .01 A in the presence of an excess of potassium cyanide. With a current liberating .8 c. c. of oxyhydrogen gas a minute, and the solution containing 1.5 grams of potassium cyanide, .1162 gram of gold was deposited in from twelve to fourteen hours.

In accordance with this suggestion, the following conditions were obtained: Two grams of potassium cyanide were added to a solution of gold chloride containing .1256 gram of metal and palladium chloride equivalent to .1 gram of metallic palladium. This was diluted to 250 c. c. The current used was N. D_{175} = 0.06–0.09 A and V = 2.5. The temperature during the decomposition was 65°. In five hours the current was raised to 0.09 A. The gold was found to be completely deposited and free from palladium.

RESULTS.

Gold.	Palladium.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Gold Found.
gram.	gram.	grams.					hours.	gram.
0.1256	0.1	2	125 c. c.	N. D_{100}=0.06–0 03 A.	2.5	65°	6	0.1250
0.1256	0.1	2	250 c. c.	N. D_{175} 0.06–0.09 A.	2.5	65°	6	0.1257

Gold from Copper.

In the report referred to, the separation of gold from copper in cyanide solution took place with a current liberating .8 c. c. of oxyhydrogen gas at the ordinary temperature in about twelve hours.

It was found that by heating the solution to 65° the precipitation was more rapid, but required more cyanide in order to keep the copper from being deposited with the gold. To a solution of gold chloride containing .1665 gram of metallic gold and copper sulphate containing 0.1 gram of copper were added 4 grams of potassium cyanide. The solution (250 c. c.), warmed to 65°, was electrolyzed with a current of N. D_{175} = 0.05–0.07 A and V = 1.7—for two and one-half hours. In this time .1667 gram of gold was obtained. There was no reaction for copper when the deposit treated with nitric acid was tested for that metal.

Results.

Gold.	Copper.	Potassium Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Gold Found.
gram.	gram.	grams.					hours.	gram.
0.1665	1	2	250 c. c.	N D_{175} 0.07 A.	1.7	65°	2½	0.1667
0.1627	1	2	250 c. c.	N. D_{175}—0.05–0.08 A.	1.9	65°	3	0.1627

Gold from Nickel.

The conditions under which this separation is made are similar to those obtained *under* the separations of silver and mercury from nickel. The solution of gold chloride used was equivalent to .1610 gram of metallic gold, and nickel nitrate contained 0.1 gram of nickel. They were converted into their double cyanides by the addition of 4 grams of potassium cyanide. A current of N. D_{100} = 0.05 A and V = 1.5 was passed through the solution (125 c. c.) at 60° for six hours. The gold on examination contained no nickel.

RESULTS.

Gold.	Nickel.	Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Time.	Gold Found.
gram.	gram.	grams.					hours.	gram.
0.1567	0.1	4	125 c.c.	$N.D._{100}$=0.05 A.	1.7	65°	7	0.1567
0.1610	0.1	4	125 c.c.	$N.D._{100}$=0.05 A.	1.5	60°	7	0.1603

GOLD FROM COBALT.

More difficulty was experienced with the separation of these metals than with the preceding. Four grams of potassium cyanide were added to the solution of gold chloride and cobalt nitrate equivalent to 0.1 gram of cobalt. The current used for the deposition of the gold was N. D_{100} = 0.05 A and V = 1.7. The electrolysis was carried out at 60° C. It was found advantageous before the end to add 1 c. c. of a 20 per cent sodium hydrate solution and raise the current to 0.08 A in order to deposit the last trace of gold. In this way the gold was entirely deposited in seven hours free from cobalt.

RESULTS.

Gold.	Cobalt.	Cyanide.	Dilution.	Current.	Voltage.	Temperature.	Dilution.	Time.	Gold Found.
gram.	gram.	grams						hours.	gram.
0.1010	0.1	4	125 c. c.	N. D_{100}=0.05-0.08 A.	1.7	60°	125 c. c.	6¾	0.1612
0.1610	0.1	4	125 c. c.	N. D_{100}=0.05-0.08 A.	1.7	60°	125 c. c.	6	0.1608
0.1495	0.1	4	250 c. c.	N. D_{175}=0.05-0.08	1.7-2	60°	250 c. c.	6	0.1497

GOLD FROM ZINC.

These metals were successfully separated according to the following conditions: Four grams of potassium cyanide were added to a solution of gold chloride and zinc sulphate containing 0.1 gram of zinc. The current acting upon the double cyanides was N. D_{100} = 0.06 A and V = 2.66. The temperature of the solution was 60°. In seven hours the deposition was complete. No zinc was found with the gold.

RESULTS.

Gold.	Zinc.	Cyanide.	Current.	Voltage.	Dilution.	Temperature.	Time.	Gold Found.
gram.	gram.	grams.					hours.	gram.
0.1495	0.1	4	N. D_{100}=0.06 A.	2.66	125 c. c.	60°	7	0.1490
0.1608	1.	4	N. D_{175}=0.06 A	2.7	250 c. c.	65°	7	0.1602

GOLD FROM PLATINUM.

To the solution of gold chloride containing .1576 gram of gold and platinic chloride equivalent to .125 gram of platinum, were added 1.5 grams of potassium cyanide. The volume of the solution was 250 c. c. A current of N. D_{175} = 0.01 A and V = 2.7 was used. The temperature was 70° C. In three hours the gold was entirely precipitated. No platinum was deposited with the gold. The deposit weighed .1479 gram.

MERCURY FROM AN ALKALINE SULPHIDE SOLUTION.

In 1891 Smith made the statement that mercury obtained as mercuric sulphide, during analysis may be accurately estimated electrolytically. The sulphide was dissolved in sodium sulphide of sp. gr. 1.19 and electrolyzed with a current generating 1 c. c. of oxyhydrogen gas per minute, acting during the night. The mercury was always compact and gray in color.

In working out conditions for the determination of mercury by this method, 25 c. c. of sodium sulphide were added to a solution of mercuric chloride containing .1403 gram of mercury. This solution, diluted to 125 c. c., was electrolyzed at 70° C by a current of N. D_{100} = 0.11 A and V = 2.5. In five hours the mercury was entirely deposited. It was light gray in color. Slightly warm water was used in washing the deposit.

RESULTS.

Mercury.	Sodium Sulphide, Sp. gr. 1.19	Dilution.	Current.	Voltage.	Temperature.	Time.	Mercury Found.	Error.
gram.						hours.	gram.	gram.
0.1403	25 c. c.	100 c. c.	N_1D_{100}=0.11 A.	2.5	70°	5	0.1400	0 0003
0.1403	25 c. c.	100 c. c.	$N.D_{100}$=0.12 A.	2.7	70°	5	0.1404	0.0001

COPPER.

"Moore advises dissolving the recently precipitated copper sulphide obtained during the ordinary course of analysis in potassium cyanide, and after the addition of an excess of ammonium carbonate, electrolyze the warm (70°) solution." —*Electro-Chemical Analysis*, Smith, page 61. According to this suggestion the following conditions for the determination of copper were found to give good results: The copper sulphate solution used contained .1270 gram of metallic copper. This was precipitated as sulphide, which was dissolved in 2 grams of potassium cyanide and ammonium carbonate added. The solution, diluted to 125 c. c., was heated to 70° C. and electrolyzed with a current of N. D_{100} = 0.02–0.07 A and V = 4. In three hours the copper was completely deposited. The copper was found to weigh .1269 gram, that is .0001 gram less than the theoretical amount.

COPPER FROM NITRIC ACID SOLUTION.

Copper has also been successfully determined electrolytically in a nitric acid solution (*American Chemical Journal*, Vol. xii, p. 329). A solution containing 10 c. c. of concentrated nitric acid was diluted to 100 c. c. and electrolyzed. The current used was N. D_{100} = 0.03 A and V = 1.7. At the ordinary temperature in sixteen hours .1396 gram of copper was precipitated. The solution treated with ammonium hydroxide showed that the copper had been entirely deposited. With a temperature of 65° and a current of N. D_{100} = 0.09 A and V = 1.9 in five hours .1397 gram of copper was found, and another deter-

mination under identical conditions gave the theoretical amount of copper present.

RESULTS.

Copper.	Nitric Acid.	Dilution.	Current.	Voltage.	Temperature.	Time.	Copper Found.
gram.						hours.	gram.
0.1398	10 c.c.	100 c.c.	$N.D_{100}=0.03$ A.	1.7	cold	16	0.1396
0.1398	10 c.c.	100 c.c.	$N.D_{100}=0.09$ A.	1.9	70°	16	0.1397
0.1398	10 c.c.	100 c.c.	$N.D_{100}=0.09$	1.9	65°	16	0.1398

CADMIUM FROM SULPHURIC ACID SOLUTION.

In the *American Chemical Journal*, volume ii, page 42, Smith describes the quantitative deposition of cadmium from its sulphuric acid solution. Cadmium oxide was dissolved in sulphuric acid. The solution contained 2 c. c. of free sulphuric acid of sp. gr. 1.095.

The volume of the solution was 25 c. c. In two hours the cadmium was completely precipitated. The amount of cadmium present was .0931 gram. The following conditions were found to give good results by this method. A solution of cadmium sulphate containing .1599 gram of metal after adding 3 c. c. of sulphuric acid sp. gr. 1.09 and diluting to 125 c. c. was electrolyzed with a current of $N. D_{100} = 0.078$ A and $V = 2.61$. The temperature during the electrolysis was 65°. In five hours the deposition of cadmium was complete. The metal weighed .1604 gram.

BISMUTH.

Smith and Thomas deposited bismuth from a citrate solution which contained an excess of sodium citrate (*American Chemical Journal*, Vol. v, p. 114). Bismuth hydrate was dissolved in citric acid and sodium hydrate added to alkaline reaction. In Smith's *Electro-Chemical Analysis*, page 69, it is stated that bismuth may be precipitated from an alkaline citrate solution, and a solution containing free citric acid. The conditions under which the deposition took place are not recorded. The following

experiments were accordingly made in order to obtain the proper working conditions:

Bismuth from an Ammonium Citrate Solution.

A bismuth nitrate solution was made, adding sufficient nitric acid to the salt to prevent the formation of a basic nitrate on the addition of water. To a solution of this salt containing .1882 gram of metallic bismuth were added 3 grams of citric acid and the solution made ammoniacal. It was diluted to 125 c. c. The temperature was raised to 70° C. A current of N. $D_{100} = 0.02$ A and $V = 1.8$ was allowed to act for three hours. At the expiration of this time the current was increased to N. $D_{100} = 0.04$ A and $V = 2.3$. Finally, in order to deposit the last traces of the metal held in solution the current was made N. $D_{100} = 0.09$ A. The deposit of bismuth obtained in this way was light gray in color, very compact and adherent. In one case the current acted all night and the deposit was darker in color, but adherent and easily washed. There was a noticeable amount of the peroxide of bismuth deposited. The anode was weighed therefore before and after the electrolysis and from the weight of the bismuth peroxide found the amount of the bismuth deposited in this way calculated and added to the weight of that precipitated upon the kathode.

Results.

Bismuth.	Citric acid.	Dilution.	Current.	Voltage.	Temperature.	Time.	Amount Found.
gram.	grams.					hours.	gram.
0.1882	3	125 c. c.	N. D_{100}=0.02 (for 3 hours).	1.8	70° all night in cold.	16	0.1881
			N. D_{100}=0.04 A.	2.3			
			N. D_{100}=0.06 A.				
0.1882	3	125 c. c.	N. D_{100}=0.02 A (for 3 hours).	1.6	70°	6¼	0.1880
			N. D_{100}=0.04 A.	2			
			N. D_{100}=0.09 A.	3			
0.1882	3	125 c. c.	N. D_{100}=0.03 A.	2	65°	6	0.1819
			N. D_{100}=0.042 A.	2.58			
			N. D_{100}=0.09 A.	3			
0.1822	3	125 c. c.	N. D_{100}=0.03 A.	2	65°	6	0.1820
			N. D_{100}=0.042 A.	2.6			
			N. D_{100}=0.09 A.	3			

Bismuth from a Potassium Citrate Solution.

The solution of bismuth nitrate used contained .1777 gram. To this were added 7 grams of citric acid, followed by an excess of potassium hydrate. The solution was diluted to 125 c. c. The temperature was 70°. The current for this solution was also low at the beginning and was gradually increased to 0.09 A. The deposit of bismuth peroxide on the anode was treated as indicated in the preceding method. The bismuth was in all cases a gray, compact, adherent deposit.

Results.

Bismuth.	Citric Acid.	Dilution.	Current.	Voltage.	Temperature.	Time.	Amount Found.
gram.	grams.					hours.	gram.
0.1767	7	125 c.c.	$N.D_{100}$=0.02 A. $N.D_{100}$=0.038 A.	2.16 2.18	65°	5	0.17648
0.1777	7	125 c.c.	$N.D_{100}$=0.02 A. $N.D_{100}$=0.05 A.	2.5 3	70°	5	0.1781
0.1777	7	125 c.c.	$N.D_{100}$=0.03 A. $N.D_{100}$=0.05 A.	2.1 2.5	65°	5½	0.1774

Bismuth from a Citric Acid Solution.

Seven grams of citric acid were added to a solution of bismuth nitrate containing .1767 gram of bismuth. The solution at 70° was electrolyzed with a current N. D_{100} = 0.02 A and V = 1.8. Subsequently it was increased to N. D_{100} = 0.07 A and V = 2.6.

Results.

Bismuth.	Citric Acid.	Dilution.	Current.	Voltage.	Temperature.	Time.	Amount Found.
gram.	grams.					hours.	gram.
0.1767	7	125 c. c.	N.D_{100}=0.02 A. N.D_{100}=0.038 A.	1.8 2.6	65°	5	0.17648
0.1767	5	125 c. c.	N.D_{100}=0.02 A. N.D_{100}=0.05 A.	1.8 2.66	70°	5	0.1761

Mercury from Nitric Acid Solution.

The fact that mercury could be determined satisfactorily from a nitric acid solution appears in the *Berichte der deutschen Gesellshaft*, 19, 329. Mercuric nitrate was electrolyzed

by Smith and Knerr (*American Chemical Journal*, volume viii, page 206). There was 0.5–1 c. c. of free nitric acid present. Bright, shining deposits of .0911 gram were obtained in thirty minutes. The current used for the purpose liberated 4 c. c. of oxyhydrogen gas per minute.

In the following work 3 c. c. of concentrated nitric acid were added to a solution of mercuric chloride containing .1403 gram of metallic mercury. The solution (125 c. c.) was electrolyzed with a current N. $D_{100} = 0.06$ A and V = 2 for four hours. The temperature was 70° C. The solution in the dish was siphoned off before the interruption of the current.

RESULTS.

Mercury.	Nitric Acid.	Dilution.	Current.	Voltage.	Temperature.	Time.	Amount Found.
gram.						hours.	gram.
0.1403	3 c.c.	125 c.c.	N. D_{100}=0.06 A.	2	70°	4½	0.1404
0.1403	3 c.c.	125 c.c.	N. D_{100}=0.07 A.	1.91	70°	4	0.1406

MERCURY FROM SULPHURIC ACID SOLUTION.

It has been known that mercury could be deposited from a solution feebly acidulated with sulphuric acid for a considerable time. The current which was used generated 5–6 c. c. of oxyhydrogen gas per minute. In repeating this method for the precipitation of mercury 1 c. c. of sulphuric acid was added to a solution of mercuric chloride. A current of N. $D_{100} = 0.4$–0.6 A and V = 3.5 effected the deposition. The temperature during the operation was 65° C. The mercury was entirely deposited in one hour. It had a brilliant metallic appearance. It was washed with cold water. The mercury present in the solution was .1403 gram. The deposit weighed .1402 gram.

IRON FROM A CITRATE SOLUTION.

In 1888 Smith reported the deposition of iron from a sodium citrate solution containing free citric acid. The

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solution used was ferric ammonium sulphate, and the current acting upon the solution gave 6 c. c. of oxyhydrogen gas per minute.

The method was repeated, using a solution of the alum containing .0378 gram of metallic iron, 10 c. c. of sodium citrate, equivalent to 1.18 grams and 3 c. c. of citric acid equivalent to .059 gram, and the solution diluted to 125 c. c. With a current of N. $D_{100} = .58$ A and $V = 5.7$ in seven hours the deposition was complete. Another determination gave .0375 gram of iron, and a third gave .0379 gram. By titration with potassium permanganate the deposit was found to contain .03789 gram of iron. The carbon, therefore, in this deposit was .079 per cent.

Similar experiments were conducted, using .1035 gram of iron. The current used was N. $D_{175} = 0.8$ A and $V = 9$. The temperature was 60° during the electrolysis. The solution was 250 c. c. The deposit weighed .1046 gram. By titration of the iron 1.06 per cent of C. was found. With identical conditions, using .1280 gram of iron, .94 per cent of C. was found in the deposited metal.

RESULTS.

Iron.	Citrate.	Citric Acid.	Current.	Voltage.	Temperature.	Time.	Found.	Carbon, PerCent
gram.	grams.	gram.				hours.	gram.	
0.0378	10 c. c.=1.18	3 c. c.=.059	N. D_{100}=0.58 A.	5.7	35°	7	0.0379	0.079
0.0378	10 c. c.=1.18	3 c. c.=.059	N. D_{175}=8–1.3	9–11	70°	4	0.0383	1.1
0.1035	10 c. c.=1.18	3 c. c.=.059	N. D_{175}=8	9–11	50°	4½	0.1046	1.06
0.1277	10 c. c. 0.=1.18	5 c. c.	N. D_{100}=0.4–1.A.	7–11	50°	4½	0.1278	
0.1277	10 c. c.=1.18	5 c. c.	N. D_{100}=.8 A	7–8	50°	4½	0.1280	0.94

FROM THE PREFACE TO THE FIRST EDITION (1898).

"In too many instances the student is introduced to qualitative analysis as his first laboratory work, and this is followed by gravimetric analysis to complete a course. This plan certainly gives the beginner a distorted idea of the relative importance of analytical chemistry in the study of the science; for the beginner a knowledge of the properties of a substance, the methods of its preparation and its uses is far more important than acquaintance with methods of separation, and general illustrative experiments should, therefore, be made the foundation work in the laboratory.

"It is the belief of the author that much that is demonstrated by the teacher in the classroom may profitably be repeated by the student in the laboratory. Repetition is necessary to fix elementary principles thoroughly in the mind of the beginner. The list of experiments here offered embraces the work of this character which has been required in the author's classes during the past ten years. Most of these exercises are simple and easily performed; others are longer or more complex, and are therefore described in considerable detail, but all of them may be performed by the aid of comparatively simple apparatus, and all, it is believed, illustrate important facts or principles.

"In the descriptive part of the book the author has kept in mind the fact that it is intended for beginners, few of whom expect to become specialists in chemistry, and he has, therefore, made the presentation of matter as practical as possible. Some important substances and technical processes are described more fully than is usually thought necessary in an elementary book. No chemical theory is introduced in the earlier chapters, but

after the student has been made familiar with important principles by experiment it is gradually presented. In explaining the atomic theory an attempt has been made to show in a very elementary manner the important steps, historically, in its development. It is believed that this method will give the student the clearest insight into a subject which is, at best, hard to grasp and which is seldom mastered."

This process has certain drawbacks. A relatively high temperature is required for the breaking up of the chlorate and the reaction is somewhat slow. It may be modified, however, as follows:

Experiment 40. Mix about equal weights, a few grams of each, of potassium chlorate and manganese dioxide. Heat the mixture in a test-tube and notice that the liberation of gas, which kindles the flame on a glowing coal, begins almost immediately. The substance does not melt, but at a relatively low temperature undergoes decomposition with separation of the oxygen. This decomposition is very rapid, as may be seen by the manner in which splinters of wood, once ignited, burn at the mouth of the test-tube.

The last experiment shows us how oxygen may be prepared in quantity, which will now be tried.

Experiment 41. Mix about 25 Gm. of dry powdered potassium chlorate with an equal weight of manganese dioxide, and transfer to a dry and perfectly clean glass flask, holding 200 to 250 Cc.

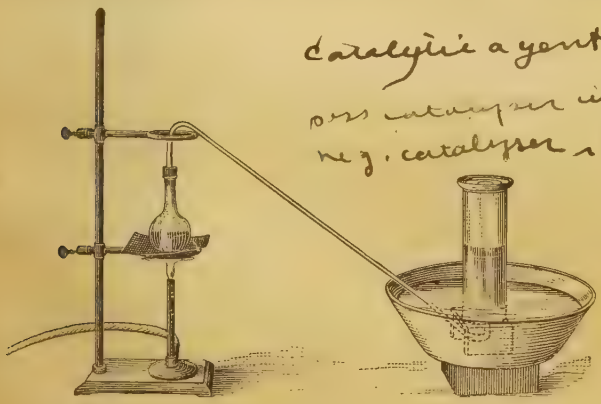

Fig. 4.

By means of a perforated stopper connect this flask with a bent delivery tube arranged as in the above figure. The further end of the delivery tube is bent upward slightly and dips beneath the surface of water contained in a pneumatic trough or earthenware bowl. The trough or bowl should be nearly filled with the water. The flask is supported on a sand-bath by means of a clamp or ring. On now applying heat by the burner, the

mixture in the flask soon becomes hot and begins to decompose as shown by the escape of bubbles of gas from the end of the delivery tube.

Method of Collecting the Gas. The gas is most readily collected by displacement of water, and the directions given for this operation here will answer for many later experiments. Have at hand several wide mouth bottles, holding about 250-400 Cc. each. Fill them *quite full* with water and then cover them with squares of glass in such a manner as to exclude all air bubbles. When this is done each bottle may be inverted by holding it with one hand, while the plate of glass is pressed down with the other. The mouth of the bottle in this position is brought beneath the surface of the water in the trough and the plate removed. The bottle remains full, its contents being held up by the atmospheric pressure, and this remains true in whatever position the bottle stands, provided its mouth is always beneath the surface of the trough water. It may therefore be held just over the end of the delivery tube from the flask, and so catch the gas bubbles as they ascend. Instead of holding the collecting bottle in the hand it is much better to support it on a bridge of galvanized iron, which has a perforation in its center about 2 centimeters in diameter. The bubbles can pass through this opening into the bottle above. When the bottle is full of gas move it to one side, its mouth still beneath the surface of the water, close with the square of glass and then lift it out of the water and stand on the table in an upright position. If the plate fits the bottle well, the gas will not soon escape. Now bring, in the same manner, other bottles of water over the end of the delivery tube and collect enough gas for all the experiments given below. The first bottle of gas collected may be contaminated by air from the generating flask, but the others should contain nearly pure oxygen. On completing the experiment the delivery tube should be taken from the water before the lamp is removed. Why?

With the bottles of oxygen collected as just explained, the student is ready to make some simple experiments to illustrate important properties of the gas.

Potassium chlorate furnishes 39.2 per cent of its weight of oxygen when completely decomposed. At the ordinary temperature 1 Gm. yields about 300 cubic centimeters of gas. For the preparation of quantities of the gas a copper retort is commonly employed, and from this, on liberation, the gas is led into a large reservoir or holder. For certain purposes the gas requires some purification, unless made of absolutely pure materials. The purification can be easily effected by allowing the

gas on leaving the generating retort to bubble through a wash bottle containing a solution of potassium hydroxide. The arrangement of generator, wash bottle and gas holder is shown in Fig. 5.

One hundred grams of the chlorate mixed with an equal weight of manganese dioxide will furnish 30 liters of gas. A little of this should be wasted, however, to drive the air from the retort and wash bottle at the beginning of the operation.

Before attempting to heat a large quantity of the mixed chlorate and black oxide, as explained above, a trial should always be made with a small quantity in a

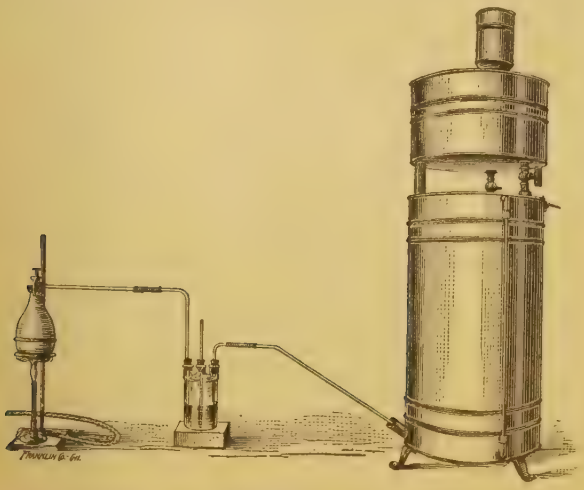

Fig. 5.

test-tube. The black oxide has been occasionally found adulterated or accidentally mixed with charcoal or other form of carbon, and dangerous explosions have resulted from the careless use of such a product. The test-tube experiment would disclose such impurity if present.

In the tests made in some of the last experiments it was discovered that the gas supports combustion well, as

shown by the rapid and brilliant burning of the splinter. A similar phenomenon is shown in the next test.

Experiment 42. Attach a piece of charcoal to a bent wire, bring it to a glowing condition in the lamp flame, and plunge it quickly in a bottle of the gas. It burns brilliantly, throwing off showers of sparks. Pour some lime-water in the bottle at the end of the reaction, close with a glass plate and shake. A white precipitate is formed, owing to the combination of a constituent of the lime-water (calcium hydroxide), with the gas produced by the combustion of the charcoal. The gas is carbon dioxide. The precipitate consists of calcium carbonate.

This experiment gives us a typical example of what is termed combustion. The oxygen in the bottle goes into intimate union or chemical combination with the hot charcoal, with production of a much higher temperature and ultimate destruction of the whole of the charcoal if the volume of oxygen is large enough. This union of the gas with the charcoal is attended by the escape of heat, and evidently intense heat, as indicated by the sparks. When carbon combines with pure oxygen gas, as in this case, the product formed is always carbon dioxide and this substance may be always recognized by the precipitate it yields with clear lime-water. It will be shown later that carbon dioxide is formed by many other reactions.

Other bottles of the oxygen remain with which the following experiments may be made:

Experiment 43. Melt a small amount of sulphur in a *deflagrating spoon* (a small brass spoon with a long wire handle bent to make a right angle with the rim of the spoon), heat it until it begins to burn with a pale blue flame and then plunge it into a bottle of the gas. The sulphur burns here with a much brighter flame than in the air.

In this combustion a gas is produced which has a very strong and characteristic odor. It is an *oxide* of sulphur, a combination of oxygen and sulphur, and is called, properly, sulphurous oxide. A similar but weaker odor is noticed when some kinds of matches are burned.

The bottle should be covered with a glass plate so that the contents may be saved for another experiment.

Experiment 44. Carefully dry a *very small* piece of phosphorus between folds of filter paper, place it in a deflagrating spoon,

ignite it by holding for a second in the lamp, and thrust quickly into a bottle of oxygen. Immediate combustion takes place, an intense white light is produced, and the bottle soon fills with fumes of a substance known as phosphoric oxide. After a time these fumes settle to the bottom and sides of the bottle and mix with the moisture present. Cover the bottle with a glass plate and keep the contents for a second test.

This experiment gives a very good illustration of the strong *affinity*, or liking, of the oxygen for phosphorus. The phenomenon is very similar to that presented in the burning of charcoal, but the phosphorus-oxygen reaction is distinguished by its greater intensity.

The direction was given to heat the phosphorus to the burning point before putting it in the gas. This was done to save time rather than because of its necessity. If left to itself in dry condition in the air, *spontaneous* combustion takes place after a time. Because of this fact phosphorus must always be kept under water.

In the experiments just given, substances which are readily combustible have been burned in the oxygen gas. Other bodies burn with greater difficulty, but in a manner none the less characteristic. This is true of many of the common metals, and as an illustration we will take iron.

Experiment 45. Cut some fine soft iron wire into lengths of about 10 centimeters and wrap a dozen or more of these into a bundle; at one end of this bundle spread the individual wires a little, and around the other end twist a piece of stronger wire to serve as a handle. Heat the loose end and dip it into some sulphur. Ignite this, and as soon as it burns well remove the cover from a jar of oxygen and hold the wire down into it. First the sulphur burns with greater brilliancy and finally the iron becomes hot enough to ignite too, burning in a manner reminding one of the charcoal combustion. The sulphur is used here merely to bring the iron up to the burning temperature. With coarse wire this experiment cannot be easily performed. In this combustion the product, like the others, is termed an oxide.

After this reaction we have two substances in the bottle, but one of them is the sulphurous oxide produced by the burning of the sulphur. The iron oxide is left as a black scale or slag, which will not dissolve in water. Iron forms several other combinations with oxygen which will be referred to later.

It remains now to make some tests with the products in the bottles after the burning of the carbon, sulphur and phosphorus. The oxides of carbon and sulphur are invisible gases; that of phosphorus appears for a time as a white cloud which subsides as mentioned.

Experiment 46. To the contents of each bottle add a little water, replace the cover and shake thoroughly. Whatever is present evidently combines with the water or goes into solution. In the water in each bottle dip a piece of blue litmus paper. The color changes to red. By means of a clean glass rod take up a drop of liquid from each bottle and touch it to the tongue. The drop from the carbon bottle imparts little or no taste, while those from the others are sour. We have here a common property of the bodies usually termed acids, as most of these have a sour taste and change blue litmus paper to red. The acid formed by the addition of water to the carbon bottle is evidently very weak.

The simple experiments just detailed are exceedingly instructive. It can easily be shown that oxygen gas itself is free from sour taste and that it does not change the color of blue litmus paper. The addition of water does not alter this. The acid properties must therefore come by the union of the oxygen with the carbon, the sulphur and the phosphorus. Further, it can be shown that these oxides in the *dry* state are not acid bodies; they become such only after the addition of water. It would seem therefore that both oxygen and moisture are concerned in the production of acids, and we shall find later that in very many cases this is true. The name oxygen signifies *acid producer*, it being at one time supposed that all acids contained oxygen.

The phenomena of combustion naturally attracted the attention of the ancient philosophers, but the explanations given of observed facts were very faulty. As intimated above, Lavoisier was the first to give a correct explanation of what appears to us now as very simple. His immediate predecessors in attempting to explain combustion and oxidation were led to the doctrine that metals, in burning, *lost* or gave up something, and this thing lost was called by them *phlogiston*. The fact that these metals grew heavier instead of lighter when burned was overlooked or considered as of very little moment. The value

of the balance in chemical investigation was yet to be shown. A few scientific men, recognizing, however, the importance of the change in weight, were forced to the absurd conclusion that phlogiston was endowed with a property of levity or negative weight, so that when added to a body it made it weigh less instead of more. According to the phlogiston view metals were mixtures of a *calx* or base with phlogiston, and application of high heat in the air liberated the light phlogiston, leaving the heavy calx.

Lavoisier investigated all these points thoroughly and established the fact that when lead, iron, tin, mercury and other common metals are heated in the air they increase in weight by the absorption of oxygen; and he was able to show in several cases that the gain in weight of the metal was equal to the loss in weight of the volume of air taken.

He found, also, as shown above, that sulphur, phosphorus and several other bodies burn in air and in oxygen, producing gases, which in turn combine with water, forming acids. From his experiments he was led to believe that all acids must contain this gas, and hence he gave to it, in 1778, the name *oxygen*, or acid producer. Before this date it had been known by several fanciful names, as *vital air, dephlogisticated air,* and others.

The term *vital air* indicates the importance of oxygen in the process of life. In an atmosphere devoid of oxygen animals die almost immediately, and experiment shows that a certain proportion of oxygen must always be present to preserve life. It has been mentioned that the atmosphere in which we live contains about 20 per cent of oxygen. With a proportion notably below this, respiration in the higher animals becomes difficult; if it falls to a certain point, death must follow. More will be said on this question later.

The oxygen taken into the lungs from the air serves for the combustion of carbonaceous substances in the tissues. Here, as in our simple experiments, carbon dioxide is formed, and this is thrown off from the lungs in the expired air. As the carbonaceous matters burned

are very complex in structure, several other products are produced, some of which are excreted by the lungs, while others are thrown off by the kidneys or through the skin. In this combustion within the body, as in all others, heat is produced and the normal high temperature of animals is thus seen to depend on chemical combination or oxidation.

Conditions of Oxidation. Some substances combine with oxygen at the ordinary temperature, and if left exposed to the air burn or become quickly corroded. The presence of moisture in many cases greatly assists this spontaneous combination with oxygen, as is well illustrated by the rusting of iron in moist air. For other substances a certain elevated temperature must be reached before combination with oxygen will follow. Our experiments have shown that sulphur and charcoal burn readily in oxygen, but only after previous heating to what is called the kindling temperature. It is a well-known fact that at the ordinary temperature these two bodies are perfectly stable, showing no tendency to oxidize.

When combustible bodies are heated to the kindling temperature in air or oxygen and burn, a certain definite amount of heat is always liberated. A gram of pure carbon burning in a sufficient supply of oxygen liberates a constant number of *units of heat*, which term will be explained later. The amount of heat liberated by the combustion of a gram of sulphur is much less than that formed from a gram of carbon, but is still a constant. The following short table gives in round numbers the units of heat liberated by combustion of 1 gram of the substances named, in pure oxygen.

Hydrogen	34,000 units.
Carbon	8,000 "
Sulphur	2,300 "
Phosphorus	5,700 "
Zinc	1,300 "
Iron	1,570 "
Tin	1,230 "
Copper	600 "

Provided the end product is the same the amount of heat liberated is a constant whether the oxidation be rapid or slow, but the *temperature* reached by the burning body depends on the rapidity of the combustion. In slow oxidation, as in the rusting of a piece of iron, the elevation of temperature is not perceptible; but in rapid combustion heat enough may be liberated to melt the oxide formed. In the former case the heat liberated is dissipated by radiation or conduction, while in the second case the reaction is so rapid that little time is given for loss in this way. Hence the elevation of temperature which follows.

The subject of the heat of combustion is a very important one in many scientific investigations, and also in the measurement of the calorific value of fuels. A knowledge of the heat of combustion of a number of simple substances makes it possible to calculate the amounts of heat which will be liberated in the combustion of given weights of fuels of known composition.

Physical Properties.—One liter of oxygen, measured at a temperature of 0°C. and under a pressure of 760 Mm. of mercury (the so-called standard temperature and pressure), weighs 1.4295 Gm. Referred to dry air its specific gravity is 1.1056. It is but slightly soluble in water, 1 volume of the latter dissolving 0.041 volume of oxygen at the standard temperature and pressure. Oxygen may be liquefied at a temperature of —118° at a pressure of 50 atmospheres.

Uses of Pure Oxygen. At the present time oxygen gas as made by the chlorate process is employed for several purposes. It is made for inhalation to a slight extent, and for this purpose must be carefully purified. Much larger quantities are made for combustion with hydrogen or illuminating gas in the production of the "calcium," "lime" or "Drummond" light. Oxygen gas is employed on a still larger scale in several manufacturing operations. Here it is made by other processes which need not be explained in this place. It is now an article of commerce and in large cities can be obtained in any quantity desired compressed in strong iron cylinders.

OZONE.

Occurrence. Along with the oxygen in the atmosphere several other so-called oxidizing substances are known to exist in small amount. One of these is a peculiar form of oxygen itself and is called ozone. It must be remembered, however, that the trace of this substance in the air is so minute that tests for its presence often fail.

History. The peculiar odor noticed in the neighborhood of a plate electrical machine in action was long ago remarked. In 1785 Van Marum called attention to the fact that the same odor is developed by the passage of electric sparks through pure oxygen, and showed that the gas so acted upon has the power of immediately tarnishing a clean surface of mercury. He found also that a decrease in the volume of oxygen taken follows. In 1801 Cruikshank observed that in the electrolysis of water acidulated with sulphuric acid a peculiar odor is developed at the positive pole. Of the nature of the substance having this marked odor neither he nor Van Marum had any knowledge. It was reserved for the German chemist Schoenbein to publish the first definite details touching the production and properties of this new body, which he did in 1839 and 1840. Schoenbein showed that by the passage of electricity through air or oxygen, in the electrolysis of water acidulated with certain acids and in the oxidation of moist phosphorus the same substance is formed, to which he gave the name *ozone*. The true composition of the gas was not recognized immediately. A number of important investigations, extending through fifteen years, were required to fully settle it to the satisfaction of all.

Preparation. By special methods we can produce ozone in the laboratory, although not easily in large amount. It will suffice here to illustrate this fact by a very simple experiment.

Experiment 47. Scrape the surface of a stick of phosphorus, about 5 Cm. long, *under water*, so as to expose the pure substance, free from coating or incrustation. Next pour some luke-

warm water into a tall beaker or wide mouth bottle to a depth slightly less than the thickness of the scraped phosphorus. Then transfer the latter to the beaker or bottle and see that the surface is exposed to a slight extent above the water to the oxidizing action of the air. Cover the vessel with a piece of glass and allow it to stand some time; five minutes is usually sufficient. Meanwhile prepare a test for the ozone, and this can be done for the present instance in the following manner. Dissolve a small crystal of *pure* potassium iodide in distilled water and into this solution stir a little starch. Rub the starch with a glass rod to break up any lumps formed and then gradually heat to boiling. This makes a paste in which the potassium iodide exists dissolved. Into this paste dip some small strips of filter paper and then suspend these in the vessel in which the phosphorus was left in contact with the moist air. If the experiment has been properly performed the paper will turn blue, indicating ozone formed.

The following explanation must be given of the above experiment. Potassium iodide is a substance which is not decomposed either in the dry state or in solution by ordinary oxygen, but it is decomposed by other substances, among which is ozone, with liberation of one of its constituents—iodine. The iodine forms a deep blue color with starch paste. If, therefore, we have a mixture of potassium iodide and starch paste and if from any cause this becomes blue, we know that some strong decomposing agent has acted on the compound, the potassium iodide, setting free its iodine. In the present case the paper turns blue because the air in the bottle contains a small amount of ozone formed by the action of the phosphorus on the moist air. The ordinary oxygen has not the power of producing this blue color.

This is an illustration of one of the many decompositions which the ozone gas can effect. It is especially active in breaking up organic matters, oxidizing or burning them in a certain sense. Ozone in the atmosphere is supposed to have the action of a purifying agent in destroying decaying animal and vegetable matters.

What is commonly called ozone test-paper is prepared by covering good book paper with a paste of

Water	1,000	parts.
Starch	50	"
Potassium iodide	5	"

The potassium iodide is dissolved in a small amount of the water in a porcelain dish. Into this solution the starch is stirred and rubbed with a pestle until it forms with the water a uniform creamy liquid. The remainder of the water is then added, and the whole is heated, with constant stirring, on a water-bath until the starch is converted into a smooth paste free from lumps. This hot paste is spread over white paper by means of a soft flat brush, and then the paper is hung up to dry in an atmosphere free from oxidizing gases. The dried paper, cut into small pieces, may be kept almost indefinitely in stoppered bottles. When used as a test for ozone in the air, a small piece is moistened and hung up in the atmosphere in question. It is used as a test for other substances, as will be shown later.

Larger quantities of ozone may be made in so-called ozone generators. These are forms of apparatus in which a current of oxygen may be passed between metallic plates connected with the terminals of an induction coil. The silent discharge across the intervening space converts a part of the gas into ozone. But the reaction is always far from complete, unless the product is absorbed by potassium iodide solution, or something else, as fast as formed.

Ozone has been shown to be formed by the condensation of ordinary oxygen in a peculiar manner, which will be referred to later. In this condensation 3 volumes of oxygen yield 2 of ozone. At a temperature of 300° C. this condensed product is completely decomposed, common oxygen resulting.

The oxidizing action of ozone is powerful, many organic substances being quickly destroyed by it. As a bleaching agent it is many times as strong as chlorine. In the older literature (since 1850) it was considered as the most powerful natural purifying agent in the atmosphere, but it is now generally admitted that most of the effects ascribed to ozone in the air are due to a related body, the peroxide of hydrogen, which will be described later, or to nitrous acid, which is present in small traces.

Technical Uses. Because of the marked reduction in the cost of the electric current it is now possible to apply it in the large scale production of ozone for certain practical purposes. Among these the most important are the purification of water for household purposes, and bleaching.

HYDROGEN.

This is a gaseous element of the highest importance from many standpoints.

Occurrence. As a free substance it is found in nature in traces only, but is one of the common elements in combination, constituting one ninth by weight of water and an important fraction of most animal and vegetable substances.

History. When iron and zinc are dissolved in dilute acids an inflammable gas is evolved. This fact was observed by some of the alchemists, but received no explanation from them or their followers. Cavendish, in 1766, published an investigation of the subject in which he describes the gas as *inflammable air*. Later he considered it as identical with pure phlogiston, because it was found capable of regenerating pure metals from the calces referred to under oxygen, and this view was held by many others. Following up his experiments, Cavendish found with considerable accuracy the amount of the gas which may be liberated from acids by given weights of several metals. In 1781 he found that water is composed of inflammable air and dephlogisticated air, but at the time he apparently failed to realize the importance of his discovery. In 1783 Lavoisier gave the first clear explanation of the composition of water and proposed the name hydrogen for the inflammable air of Cavendish. About this time it was found that hydrogen may be obtained by the action of certain metals on strong alkali solutions as well as on acids.

Preparation. We are able to separate hydrogen from its compounds by many simple reactions. In illustration of these we will consider first the decomposition of water.

It has been stated before that water is a compound of hydrogen and oxygen, and in separating them we must overcome the strong affinity which holds them together. This may be conveniently done by passing a strong current of electricity through the water slightly acidulated with sulphuric acid. Certain metals brought in contact with water are also able to separate the hydrogen through the attraction they have for the oxygen. The following experiment will show how this separation may be effected at the ordinary temperature:

Experiment 48. Drop a small piece of sodium, *not larger than a pea*, on the surface of water contained in an earthenware bowl. As the metal is lighter than water it floats, but as it does so a decomposition goes on indicated by the escape of a gas with a sound reminding one of the escape of steam. On striking the water the sodium melts and assumes the globular form. It soon becomes evident that in the reaction between the two the sodium is worn away, as the globule grows small and finally disappears. While the gas is escaping bring a small flame in contact with it and observe that it ignites and burns readily with a yellow color. Very often the gas ignites spontaneously. In performing this experiment it sometimes happens that the sodium globule flies into small bits which are scattered in all directions. The face should not be held over the bowl, therefore, when making the test.

Sodium is a light, silver white metal which is kept under rock oil. When a piece is taken out for this experiment it is cut to the proper size and wiped free from the oil by means of filter paper. The liberated gas may be collected in a bottle or test-tube and examined. To do this, fill the bottle or tube with water and invert it in the bowl in the usual manner. Then wrap a bit of clean dry sodium in filter paper or wire gauze, and by means of tongs bring the pellet so enclosed under the mouth of the bottle or tube, held for the purpose just below the surface of the water in the bowl. The decomposition takes place as before, but the gas ascends into the receptacle, and may be tested as explained later. The beginner is not advised to make this experiment. The yellow color of the flame is not characteristic of hydrogen, but of the vapor of sodium burned with it.

Experiment 49. Repeat the last experiment, using a small piece of potassium instead of sodium. Observe the same precautions. The flame is now violet.

In both of these experiments hydrogen gas is set free and a certain amount of water has been converted into something else. The character of this is disclosed by two simple tests. First, by means of a glass rod touch a little of the water to the tongue; a sharp caustic taste will be noticed. Then dip a piece of red litmus paper in it and notice the change of color to blue. This is evidence of the presence of alkali. The same evidence is given by the deep red color produced when a few drops of alcoholic phenol-phthalein solution are added to the water. It appears, therefore, that in this experiment with the water hydrogen gas is liberated, while an alkali substance is formed.

Sodium and potassium are not the only metals which decompose water in the cold, while at a high temperature the reaction is possible with many others, as is readily shown. The usual method of procuring hydrogen for experiment depends on the decomposition of some acid by means of a metal. In an experiment described in the last chapter it was shown that when dilute sulphuric acid is poured over zinc in a beaker the metal gradually dissolves with evolution of gas. This gas is hydrogen and the experiment may now be arranged to collect and test it.

Experiment 50. Arrange a gas generating bottle as shown in the cut, Fig. 6. The bottle should hold about 250 Cc. and be closed with a doubly perforated stopper. Through one perforation the stem of a funnel-tube passes while the gas is led out through a "delivery tube" from the other. Put some granulated zinc in the bottle, insert the stopper with the funnel-tube and delivery tube, add some water and then some dilute sulphuric acid so as to about one third fill the bottle and cover the lower end of the funnel-tube. An evolution of gas soon begins, and if the end of the delivery tube is brought under water the gas passes through and may be collected as in the case of oxygen. Therefore arrange several bottles for the collection of gas as there described, and after it has bubbled through the water a few minutes, allow them to fill with the gas. When filled remove them by aid of a glass plate but keep the mouths of the bottles now down, because the gas is much lighter than air. When several bottles are filled their contents may be tested.

1 part acid
4 " water

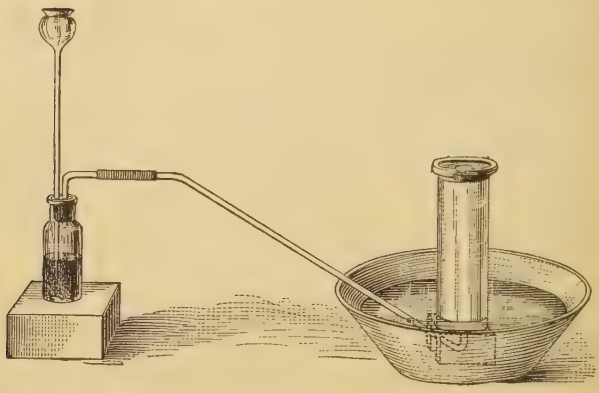

FIG. 6.

Experiment 51. Lift one of the bottles from the table, mouth still down, and thrust up into it a lighted taper or splinter of burning wood. As the light goes into the bottle it is extinguished but a flame appears at the mouth of the bottle, from the ignited hydrogen. The gas, therefore, burns, but the combustion on the end of the taper or splinter is checked, because, as shown before, oxygen is necessary for this and the bottle contains hydrogen. The hydrogen itself, at the mouth of the bottle, enters into combination with the oxygen of the air.

Experiment 52. Invert one of the filled bottles, holding the mouth now up, remove the glass plate and bring a flame to the gas. It will ignite with a slight report and burn in the bottle, as the heavier oxygen of the air tends now to settle and mix with the hydrogen. In nearly all cases the flame shows some color. This is not characteristic of the hydrogen but of various impurities with it or on the surface of the glass. The flame from pure hydrogen has a slight blue tinge only.

Experiment 53. The relative lightness of hydrogen may be readily shown by pouring it *upward* into a bottle filled with air. Use one of the bottles of hydrogen still standing on a glass plate. Lift it with one hand, and turn it so that its mouth is brought under and near that of the air-filled bottle of the same size. After a minute or two hold the upper bottle to a flame, when a sharp report shows the presence of hydrogen. The lower bottle still contains some of the gas, which can be shown in the same manner.

It will be seen later that certain gases heavier than air can be poured *downward* from one vessel into another, as in the case of water. This is true of carbonic acid gas and chlorine, for instances. In the above experiment the light hydrogen ascends, and a certain amount of the air in the upper bottle is forced out by it. The displacement is not perfect, however, as was shown by the manner of the explosion of the gaseous mixtures in the two bottles above.

Hydrogen from Other Sources. While hydrogen is commonly prepared as just shown, it may be made by the action of certain metals on alkali solutions. Aluminum wire, for instance, decomposes a solution of potassium or sodium hydroxide very readily, especially when aided by heat. The reaction may be carried out in a test-tube, and the character of the escaping gas determined. The same alkali solutions are decomposed by other metals also.

These reactions have practical value, as in certain investigations it is desirable to liberate hydrogen without the use of an acid, and the alkali methods may then often be applied.

Hydrogen is also easily liberated from water by the passage of the electric current, as intimated. This will be illustrated later by an experiment to determine the composition of water.

It has been shown that sodium and potassium decompose cold water with liberation of hydrogen. At a higher temperature the same decomposition may be effected by other metals. When steam is passed through an iron or porcelain tube containing iron turnings, and heated to a very high temperature in a gas furnace, it is decomposed, the hydrogen being set free, while the oxygen remains in combination with the iron, forming an oxide of iron. This experiment is easily carried out in the apparatus illustrated by the figure below. Water is boiled in a flask to the left. The steam generated passes into the tube resting over a number of burners in the furnace, while the liberated hydrogen is collected in a jar beyond. By

filling the tube with charcoal instead of with iron turnings, a somewhat analogous decomposition takes place. We obtain now hydrogen mixed with *oxides of carbon*, as the carbon combines with the oxygen of the water to form these bodies, which are gases.

The last decomposition is a very important one, as it is the basis of the process commonly followed in the man-

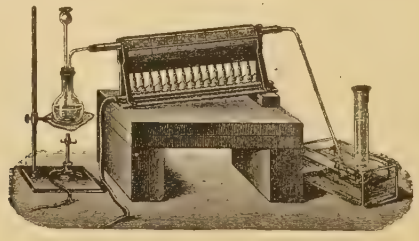

Fig. 7.

ufacture of water gas, generally used at the present time. It will be fully described later.

Diffusion of Hydrogen. Because of its extreme lightness this gas is very suitable for showing an interesting property of all gases, viz.: that of *diffusion*. Two gases separated from each other by a porous partition—a thin plate of plaster of Paris, for instance—will in time mix with each other, as both pass through the porous substance. The rates of diffusion or passage of the gases bear a close relation to their specific gravities or densities. It has been found that the velocity of diffusion is inversely proportional to the square root of the density of a gas. From this it would follow that hydrogen must diffuse 4 times as fast as oxygen and 3.8 times as fast as air, as the densities of the gases stand to each other in the relation, 1 : 16 : 14.45. A simple proof that hydrogen moves much more rapidly than air is given in the following experiment:

Experiment 54. From a piece of glass tubing having an internal diameter of a centimeter or more, cut off a length of about twenty centimeters. Dip one end of this into some soft plaster

of Paris, so as to take up a plug about one centimeter in thickness. Set the tube aside for this to harden, which will require some hours. Then fill it with hydrogen gas by displacement of the air, and immediately stand it in upright position in a beaker of water in such a manner that the open end is covered to a depth of several centimeters. It will be observed that the water ascends in the tube and finally reaches a position much above the level of the water in the beaker. It then recedes slowly and in time the level corresponds to that outside.

In the first stage of this experiment the water ascends because the hydrogen passes out through the porous plug much faster than the air can enter. The maximum position of the water is reached when the rates of motion in opposite directions are equal, after which the column of water falls because the volume of gas entering the tube is now greater than that leaving it. Many porous stones may be used to exhibit this phenomenon.

Reducing Power of Hydrogen. By this we understand the property which hydrogen possesses of abstracting oxygen from certain compounds, forming with it water. The term is used also in a broader sense but in this place the limited usage only will be considered.

It will be shown later by experiment that when hydrogen gas is passed over the oxides of copper or iron, heated to a high temperature, the oxygen is taken and the metal left in the free state. Other metallic oxides may be reduced in a similar manner.

This reaction is one of the highest importance and is frequently employed in the laboratory for several purposes. An illustration will be given in the next section.

An animal placed in an atmosphere of hydrogen would soon die, but this would follow from asphyxiation rather than from any poisonous property of the gas. In an atmosphere of 4 parts of hydrogen and 1 part of oxygen animals live apparently as well as in ordinary air.

Physical Properties.—Hydrogen is but slightly soluble in water, 1 volume of the latter dissolving of the gas 0.0193 volume at a temperature of 0°C., and under a pressure of 760 Mm. of mercury. Several metals possess the power of absorbing hydrogen in considerable quantity. In the case of the metal palladium this power is

very marked. The cold metal absorbs about 375 times its volume of hydrogen, while at a red heat nearly 1,000 volumes are absorbed.

Under standard conditions 1 liter of pure hydrogen weighs 0.0900 Gm. It has been condensed to a colorless liquid at a temperature below — 242° C., and under normal pressure has a boiling point of — 252°.

WATER.

Occurrence. The student is familiar with the natural occurrence of water in the seas, lakes, rivers, etc. The purification of water by distillation has been referred to already, and further details of practical processes will be given later.

History. In the preceding section it was explained that the exact composition of water was first suggested by the experiments of Cavendish, while Lavoisier's work proved the fact conclusively. Careful investigations undertaken by Gay Lussac and Humboldt were published in 1805, and these confirmed the work of Lavoisier and showed that exactly two volumes of hydrogen combine with 1 volume of oxygen to form water.

Some experiments will now be given to illustrate methods of finding this ratio.

Composition of Water. The presence of hydrogen in water was suggested by the experiment in which metallic sodium was used to decompose water. Other metals, as intimated, behave in a similar manner. At a high temperature, water is readily decomposed by iron turnings with liberation of hydrogen, which has been referred to already. A still more convenient method of decomposition is by means of the electric current, which will be experimentally shown.

Water in absolutely pure condition is not a conductor of electricity and therefore in this form is not decomposed by it. But by the addition of a little acid to water it becomes in effect a moderately good conductor, and the current which may now be made to pass through brings

about decomposition. Acids are not the only substances which when added to water render it a conductor, but for our purpose they are the most convenient. If two plates or strips of thin platinum foil, attached to the opposite poles of a galvanic battery of several Bunsen or Leclanché cells, be dipped in a beaker of acidulated water, gas bubbles will be seen to ascend from the surface of each plate. If these plates be supported beneath two tubes filled with water the gas bubbles will pass up into them and displace the water. After a time the contents of each tube may be tested. If the tubes are so placed that they collect all the gas given off from each plate in a given time it will be noticed that one volume is almost exactly twice the other, and that the tests of the larger volume show it to be hydrogen, while the smaller volume gives the tests characteristic of oxygen. Several special forms of apparatus have been devised for this experiment of which the one now to be described is very convenient. It should be remembered, further, that this water decomposition is a *secondary* phenomenon; the acid or other substance added seems to be first decomposed, and the products formed effect then the water decomposition.

Experiment 55. Arrange the apparatus as shown in the next figure (Fig. 8). As seen it consists essentially of a long U tube, the two limbs of which are closed on top by ground glass stopcocks. From the bottom of the bend a tube passes backward and then upward, ending finally in a wide bulb or reservoir. Inside of each limb of the U tube, just above the bend, there is a thin, platinum plate, which is connected with a short platinum wire passing through the glass and ending in a loop just outside.

By opening the stopcocks on the U tube, the apparatus may be filled with acidulated water, to this level, by pouring into the bulb tube. The stopcocks are then closed. (Water containing about 5 per cent of sulphuric acid is suitable for the purpose.) The apparatus is now ready for the actual experiment which is begun by attaching the copper wires from a good battery to the platinum loops described above. Almost immediately gas bubbles form on each plate and escape up into the tubes above. As the plates are situated above the bend of the U, the gases cannot mix on liberation, but must remain separate. In a few minutes it becomes apparent that the volume of the gas liberated from the plate connected with the negative pole of the battery, the pole connected with the zinc, is practically twice the volume liberated at the other pole.

Allow the experiment to continue until the larger volume fills the limb down to the platinum plate. It will be observed that as the gases collect the liquid is forced down and then up into the bulb tube, and further that the diminution of the volume of liquid itself is not great. In fact, not more than a small drop of the liquid undergoes decomposition to form the relatively large gas volume.

The nature of the gases in the two limbs may now be tested.

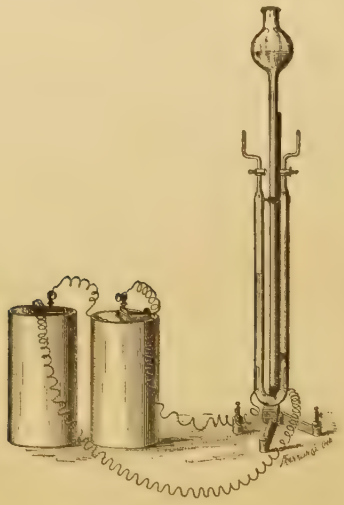

FIG. 8.

To this end wipe off the tips above the stopcocks, and free them as far as possible from liquid by means of bibulous paper, then light a small taper or splinter, hold it over the limb with the larger volume and carefully open the stopcock. The pressure of the liquid in the bulb tube will force the gas out, and this burns in a manner characteristic of hydrogen, on coming in contact with the small flame. Over the other limb hold a glowing splinter. On opening the stopcock the gas which streams out gives the behavior characteristic of oxygen. According to this experiment it would appear that water may be decomposed into two volumes of hydrogen and one of oxygen.

By repeating the above experiment carefully with accurate apparatus it can be shown that one volume is a little more than twice the other. The oxygen volume is

relatively small because this gas is more soluble in the liquid than is the hydrogen, and also because a little of it is changed into ozone in the reaction. Both of these facts have been referred to already. If precautions are taken to avoid the production of ozone and if the solubility of the oxygen is diminished by working at a high temperature then the two volumes will be found to be liberated in the exact proportions of 2 : 1.

As carried out, the last experiment could not be regarded as conclusive, as not all of the liquid was decom-

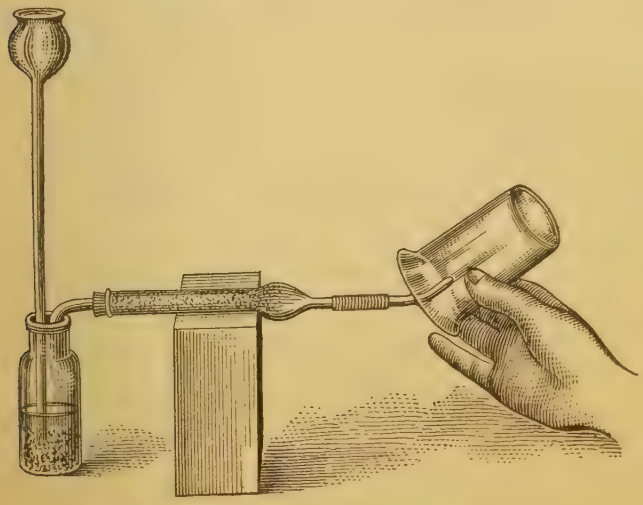

Fig. 9.

posed. But the experiment may be repeated as often as desired with the water remaining after each test until its volume becomes quite small. The result of the electrolysis is the same in all cases.

Further information concerning the composition of water is given by the following experiments.

If, as suggested by the foregoing, water is composed of hydrogen and oxygen gases we should be able to produce water by the combination of these two substances.

The experiment may be readily made and according to several plans.

Experiment 56. First, we may make a very simple experiment with the apparatus illustrated above. To the common hydrogen generator is attached a so-called drying tube, which contains some substance to absorb moisture from the gas. Calcium chloride is often used for the purpose. The generated gas after passing through the drying tube reaches the air by means of a narrow tube with a fine opening. The hydrogen gas, *after having passed long enough to expel the air,* is lighted at this opening and burns with a small hot flame. If now a cold dry beaker be held, mouth down, over this flame a deposit of moisture immediately collects on the cold surface of the glass. This must be formed by the union of the hydrogen with something in the air.

That this substance from the air is the oxygen may be shown by trial with the pure gas.

Given volumes of the two gases may be combined directly by aid of an electric spark and the result noted, when it will be found that exactly two volumes of hydrogen unite with one volume of oxygen. For our purpose it will prove more convenient to make the determination in another manner, somewhat less direct, but equally conclusive. Instead of combining the hydrogen with pure oxygen we can allow hydrogen gas to act on some substance containing oxygen in combination, under such conditions that the substance will decompose, giving up its oxygen to the hydrogen. In such a case hydrogen acts as a *reducing agent,* as was explained some pages back, and the oxides of copper and iron are good illustrations of substances which may be decomposed in this manner. The oxide of copper is a compound easily made in condition of great purity so that there is no doubt regarding its exact composition and the proportion of oxygen it contains. The experiment which the student is able to make with this substance is a *qualitative* one, but the modifications necessary to make it *quantitative* will be suggested.

Experiment 57. Arrange the apparatus as shown in the next figure. It consists of a hydrogen generator and a tube following it filled with calcium chloride to dry the gas. Then follows a piece of hard glass tubing, plain or furnished with a bulb, to contain the pure dry copper oxide to be decomposed. After the

tube of hard glass comes a bent, or U tube, to catch the products of the reaction to be described. This U tube is immersed in a beaker of cold water, and in turn is joined to a second small calcium chloride tube. The connections must all be made with perfect, sound corks, which fit with absolute accuracy. The apparatus being ready, and the hard glass tube charged with 10 to 20 Gm. of the copper oxide, we begin the experiment by generating hydrogen in the usual manner by the action of dilute sulphuric acid on zinc. The gas, given off in the moist condition, is dried as it passes through the calcium chloride tube and then enters the combustion tube, from which it displaces the air. After the gas has passed some minutes through the apparatus the flame of a Bunsen burner is applied to the combustion tube imme-

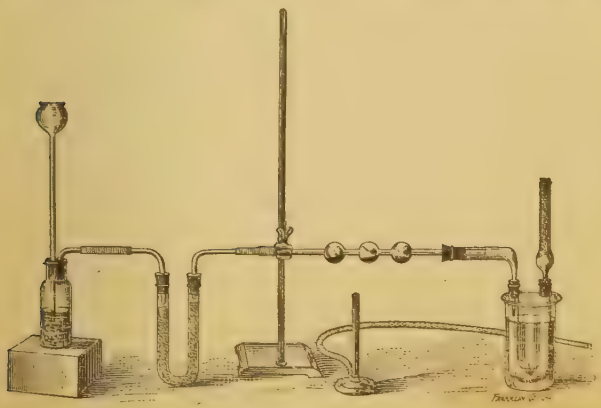

FIG. 10.

diately under the portion of the oxide of copper nearest the generator. The heat must be very carefully applied at first to avoid cracking the hard tube, which can be best prevented by having the flame low and by moving it to and fro along the tube. After a few minutes stronger heat may be applied. It will soon be noticed that vapor ascends from the black mass and that it is pushed forward by the pressure of the hydrogen toward the U tube, and also that in a short time the heated oxide above the flame glows as if on fire. We have here the stage of active reduction. It becomes presently evident that in this very hot part of the tube the oxide of copper has been converted into bright metallic copper, the color of which is very distinct. When the reaction here is complete the flame is moved onward toward the U tube and the operation continued until the whole of the black oxide has undergone decomposition. The vapors given off suggest

the formation of water, but this can be further tested in the U tube. These vapors tend to condense in the cooler part of the combustion tube itself, but the condensed product can be dislodged by careful application of the lamp heat and completely driven over into the U tube in the beaker of water. A small portion of the vapor passes through the U tube, but is intercepted by the calcium chloride tube beyond. After the completion of the reduction, that is, when the black oxide of copper has disappeared, leaving only bright metal, the heat is withdrawn, leaving the tube to cool down with the current of hydrogen still passing. Then it is taken apart and the contents of the U tube examined. The proper tests, which the student is not prepared to make at this stage of his work, however, show that the condensed liquid is water, and nothing else. It has evidently been formed by the union of the hydrogen gas with the oxygen taken, as needed, from the copper oxide.

It sometimes happens in this experiment that the water collected is slightly colored. This is due to the action of heat on the corks at each end of the combustion tube, and can be avoided by careful manipulation. The oxide of copper should be pure and free from any kind of organic dust, and should occupy the central portion of the combustion tube. This must be quite clean and dry at the beginning of the experiment. The oxide of copper may be held in proper place by means of a *loose* tuft of clean glass wool at each end.

To make the experiment perfect in all details would necessitate the complication of the apparatus to a degree which would render it unfit for our present purpose. As constructed and manipulated above it is sufficient to show conclusively that only hydrogen and oxygen are concerned in the formation of water. By the introduction of certain modifications the experiment may be made a quantitative one. It is simply necessary to provide more perfect apparatus to absorb the water formed, and weigh this accurately before the experiment. It is weighed again at the end, the *increase* in weight showing exactly the amount of water produced. The oxide of copper must be weighed before the experiment, and the residue left after it. The *loss* of weight here corresponds to the oxygen given to the hydrogen. The experiment, therefore, gives us the weight of oxygen in a determined weight of water; the difference between these two

weights represents the hydrogen, because nothing else has been used in the work.

This is a fundamental experiment upon which many skilled chemists have spent a great deal of time, for the purpose of determining with the highest possible accuracy the exact ratio in which hydrogen and oxygen combine. This knowledge, as will appear later, is of great scientific importance, as much depends on it.

We have here and above, apparently, two experiments which seem to contradict each other. Some pages back it was explained that steam passed over a hot metal is decomposed, with formation of an oxide and liberation of hydrogen. In this last experiment the reverse action is seen to follow. The seeming contradiction will be explained later.

A very satisfactory method of showing the *direct* union of the two gases in the proportion mentioned, is by means of an explosion of a mixture of the gases in an apparatus known as an eudiometer, shown in the next figure. This apparatus consists essentially of a long, accurately graduated glass tube, the divisions being usually in millimeters. Near the closed end of the tube two pieces of platinum wire are passed through the glass and sealed in so that they nearly, but not quite, touch inside the tube.

The eudiometer is filled with mercury, inverted in a reservoir of mercury, b, and clamped in position. A certain volume of pure hydrogen is now allowed to enter the tube and is accurately measured, the tube being brought to a vertical position for this purpose, and for all subsequent measurements. The illustration shows the tube in an inclined position, into which it is brought for convenience in filling.

A volume of pure oxygen over half as great is next added and the new mixed volume accurately noted. The open end of the eudiometer is pressed down on a piece of rubber under the mercury and then the tube is firmly clamped. A spark from an induction coil is caused to jump between the wires within the tube. This produces an explosion in the gaseous mixture, and when the pressure on the rubber plate is released it will be noticed that

mercury rushes up into the tube. After a time the remaining gas volume is accurately measured. A subsequent test shows that it is oxygen. If this volume is subtracted from the oxygen volume taken it will be seen that the oxygen actually used is just one half of the hydrogen volume taken. The droplet of water formed in the ex-

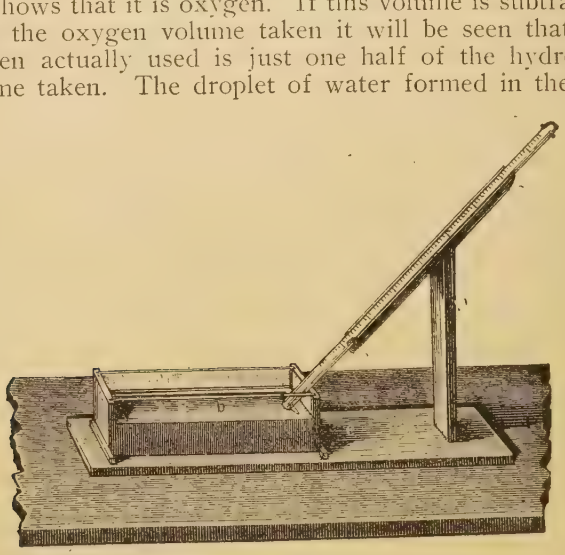

Fig. 11.

plosion is so small that its volume may be neglected in comparison with the gas volumes concerned.

In measuring the gases in this experiment certain precautions must be taken which are fully explained in a following chapter. In all such cases temperature and pressure must be accurately observed so that by reduction all the volumes may be compared under the same conditions.

Physical Properties of Water. Pure water has a constant freezing point and constant boiling point under constant conditions of pressure. It is a poor conductor of heat and is practically a nonconductor of electricity. When water at the ordinary temperature is heated it expands pretty regularly until its boiling point is reached, and by further addition of heat is converted into steam,

the volume of which is about 1,700 times that of the water. When cooled a contraction of volume follows until the temperature of 4° C. is reached. At this temperature, or more accurately, 3.95°, water reaches its smallest volume for a given weight, and therefore, its maximum density. When further cooled it expands slightly until the freezing point is reached. On conversion into ice a marked expansion takes place, 100 volumes of water at 0° yielding 109.1 volumes of ice.

Capacity for Heat. Unit of Heat. It is a matter of common experience that water "absorbs" a large amount of heat, practical application of which power is made in the hot water system of heating houses. In order to measure any amount of heat under consideration physicists have adopted what is known as a *unit of heat*. This may be arbitrarily defined as the amount of heat necessary to raise the temperature of a gram of pure water through one centigrade degree. To be scientifically correct this definition requires a slight modification or qualification, but it is sufficiently close for the present purpose. Some interesting facts have been brought out in studying the absorption of heat by water in its three forms. To illustrate these let us start with a gram of ice at 0° centigrade, that is, at its melting point. To convert this into water at the same temperature a relatively large amount of heat must be applied. It has been found that 79.5 units must be added to accomplish this. In other words, as much heat must be absorbed by the ice in melting as would be sufficient to warm 79.5 grams of water one degree, or one gram of water 79.5 degrees. This absorbed heat is usually spoken of as *latent heat*, because it is lost or hidden as far as any thermometric observation is concerned. It is used up, however, in doing a certain kind of work on the ice, that is in changing its physical condition. If we continue the addition of heat after the ice has been melted the effect now becomes visible in the increase of the temperature of the water. For each unit of heat added the temperature of the water rises one degree centigrade. Finally, on addition of 100 units of heat the water begins

to boil, and a centigrade thermometer immersed in it marks 100 degrees. Supposing the water in a vessel under constant pressure, that of the atmosphere, it is now observed that further addition of heat produces no corresponding elevation of temperature. It is a well-known fact that a thermometer immersed in pure boiling water registers a constant temperature. The heat applied is, therefore, again rendered latent as in the case of the conversion of ice into water.

Now it is used up in doing a new kind of work, the conversion of the water into steam at the same temperature. Accurate experiments have shown that about 536 units of heat are required to convert a gram of water at a temperature of 100° into steam at the same temperature. When a gram of steam at this temperature condenses it gives out the 536 units. Many of the technical applications of water and steam depend on these remarkable properties. Many other liquid and solid substances may be brought to a higher temperature than is possible with water, but for a given range of temperature not one of them absorbs nearly as much heat. A hot water bag filled with water at 60° C. will give out, as it cools down, nearly ten times as much heat as would a mass of iron of the same weight at the same temperature. The *specific heat* of iron and all other solid and liquid substances is much below that of water. This matter will be taken up again.

Boiling Point of Water and Vapor Tension. By definition water is said to boil at a temperature of 100° centigrade. But this temperature of ebullition depends on the pressure on the surface of the water, usually that of the air. If the atmospheric pressure is *normal*, that is, if it is equivalent to the pressure of a column of mercury 760 Mm. in height the boiling point is constant at 100°. At pressures below this the boiling point is below 100°, and at higher pressures it is above. In any case water boils when the tension of the vapor which it gives off is equal to the pressure of the atmosphere.

When water is heated in a confined space, as in a boiler

furnished with a weighted valve, the temperature of ebullition may become very high. Corresponding to any given pressure on the surface of the water there is a definite temperature of ebullition. Even at very low temperatures the vapor given off from water possesses a certain tension. This is shown in the table below where the tensions corresponding to certain high as well as low pressures are given. The tensions are expressed in millimeters of mercury.

Temp. Deg.	Tension.	Temp. Deg.	Tension.	Temp. Deg.	Tension.	Temp. Deg.	Tension.
1	4.909	18	15.330	35	41.78	120	1491
2	5.272	19	16.319	40	54.87	125	1744
3	5.658	20	17.363	45	71.36	130	2030
4	6.069	21	18.466	50	91.98	135	2354
5	6.507	22	19.630	55	117.52	140	2718
6	6.672	23	20.858	60	148.88	145	3126
7	7.466	24	22.152	65	187.10	150	3581
8	7.991	25	23.517	70	233.31	155	4089
9	8.548	26	24.956	75	288.76	160	4652
10	9.140	27	26.471	80	354.87	165	5275
11	9.767	28	28.065	85	433.19	170	5962
12	10.432	29	29.744	90	525.47	175	6717
13	11.137	30	31.510	95	633.66	180	7546
14	11.884	31	33.37	100	760.00	185	8453
15	12.674	32	35.32	105	906.	190	9443
16	13.510	33	37.37	110	1075.	195	10510
17	14.395	34	39.52	115	1269.	200	11689

From the table it is seen that at a temperature of 150° the tension of the vapor on the containing vessel is 3,581 millimeters of mercury, or over 4.7 atmospheres.

Water as a Standard Substance. Because of the fact that water is everywhere abundant and readily obtained in pure condition, it is well suited for use as a standard substance. It is employed in the definition of a unit of heat as mentioned above. In the construction of thermometer scales it is employed in determining two fixed points. In the centigrade or Celsius scale one fixed point is called the zero point, and represents the temperature at which water freezes. The other fixed point

is marked 100° and represents the boiling point of water at the normal pressure of the air at sea level. By definition a *gram* is taken as the weight of a cubic centimeter of pure water at a temperature of 4° C. at the latitude of Paris. By specific gravity or specific weight we understand the ratio of the weight of a given volume of substance to the weight of the same volume of pure water as the standard. In many other cases water is taken as one of the elements in comparison, but the above illustrations are sufficient.

Solvent Action of Water. Water is the best single solvent known, although for practical purposes many substances may be considered as insoluble in it. Of those which do dissolve some are much more soluble than others. One volume of water dissolves 0.041 volume of oxygen at a temperature of 0° C. and a pressure of 760 Mm., but under the same conditions it dissolves nearly 80 volumes of sulphurous oxide and about 500 volumes of hydrochloric acid gas. Some mineral substances, as gypsum, are but slightly soluble, while others, salt and saltpeter for illustrations, dissolve very largely. With increase of temperature there is in most cases a marked increase in the degree of solubility of bodies. Even such hard substances as the glass of our beakers and test-tubes dissolve to a very slight extent by long contact with boiling water. This fact is of great importance in some branches of chemical analysis.

Natural Waters. All natural water comes to the earth in the form of rain, and in this condition it is nearly pure, containing not much more than traces of dissolved gases. This is especially true of the water collected at the end of a shower, that which falls first serving to carry down the dust suspended in the air. On reaching the earth the character of the water is very speedily modified by the mineral substances which, by virtue of its solvent action, it takes up. As the rain descends it dissolves a little carbon dioxide and thus becomes a very weak solution of carbonic acid. This acid aids in the solution of limestone and other substances from the soil, and in this

way the water becomes *hard*. Hard waters are those which hold in solution relatively large amounts of certain mineral substances, principally salts of calcium and magnesium. If the soil on which the rain falls, and through which it filters or percolates, is free practically from these soluble mineral constituents, the water appearing later as a spring or brook is called *soft* water.

Some natural waters contain not over 50 milligrams of dissolved substances in one liter, while others contain in a liter many grams.

Purification of Waters. Natural waters contain substances dissolved and substances in suspension. Both may be objectionable for certain purposes, and before use water must often be freed from them. The highest degree of purification is ordinarily accomplished by distillation, the condensed steam being free from the dissolved solids and suspended matters originally present. In many cases purification extends only to a mechanical separation of suspended matters, which is accomplished by filtration through sand, charcoal or other porous substance. Finally, water is frequently treated on the large scale with something that produces in it a bulky precipitate which in settling carries down practically everything in suspension. After such precipitation, by milk of lime or alum, the water is allowed to settle thoroughly, or clarification is hastened by filtration.

HYDROGEN DIOXIDE.

Hydrogen and oxygen combine in two proportions. In one case water is the result and in the other the body known as hydrogen *dioxide* or *peroxide*.

Occurrence. This substance occurs in some atmospheres in small traces, being produced by several natural agencies. In the air it is frequently confounded with ozone, as the two bodies are much alike in their behavior with reagents.

Preparation. Hydrogen dioxide can easily be made in the laboratory as illustrated by the next experiment.

Its preparation depends on the decomposition of a solid substance, usually barium dioxide, by means of sulphuric acid.

Experiment 58. Take about 10 grams of barium dioxide in a beaker, moisten it with water and allow the mixture to stand half an hour or longer, with occasional stirring. Then add about 20 cubic centimeters of dilute sulphuric acid (1 vol. of acid to 10 of water), stir well and after a few minutes filter. The acid acts on the barium dioxide in the dry state very slowly, but if the latter has been previously hydrated by the action of water the decomposition is much more rapid. Insoluble barium sulphate and soluble liquid hydrogen dioxide result. The former is separated by filtration while the solution of the latter serves for tests.

Properties. As usually made, hydrogen dioxide is largely mixed with water, but in the pure state it is a thickish liquid with a specific gravity of 1.45. In this condition it is not stable, but decomposes at the ordinary temperature into water and oxygen gas. For this reason the substance is always kept in very dilute condition, and experience has shown that its stability is increased by having a little free sulphuric acid in the solution.

Even in dilute solution it is characterized by its strong oxidizing properties, and the numerous uses it has found in the arts and medicine depend on this fact.

Tests. Some of the reactions of hydrogen dioxide may be shown by these experiments:

Experiment 59. To a solution of the dioxide add some solution of potassium iodide. A decomposition of this compound takes place, with liberation of iodine, as is shown by the brown color of the liquid. If a little starch paste is added, it turns blue. The solution of the dioxide used in this test should be nearly neutral, that is, free from anything greater than traces of acid. This test, it will be observed, is very similar to that for ozone, given earlier.

Experiment 60. Another very interesting decomposition is shown as follows: Acidify the solution of the dioxide with dilute sulphuric acid and add to it a dilute aqueous solution of potassium permanganate, a few drops at a time. This latter solution has a deep purple color and as the drops fall into the dioxide liquid the color disappears, while bubbles of oxygen gas escape. On addition of a sufficient amount of the permanganate solution the purple color persists. The chemical reaction taking place here

is somewhat complicated and cannot be explained in this stage of the work.

The two experiments just given illustrate the marked property of producing decompositions possessed by the dioxide. This property depends on the fact, to be more fully explained later, that part of the oxygen united to hydrogen in the compound is only loosely held. It is very easily liberated and performs highly characteristic oxidation changes in consequence.

Hydrogen dioxide is used to some extent in laboratories as a reagent, but its most common applications are as a bleaching agent and in medicine. Its power of destroying pus is especially marked and many of its uses depend on this fact.

CHAPTER III.

CHLORINE AND HYDROCHLORIC ACID.—THEORETICAL CONSIDERATIONS.

We come now to the consideration of some very important substances which never occur in the free state in nature, but in many compounds are widely distributed.

CHLORINE.

Occurrence. This is an exceedingly abundant substance in combination, being one of the constituents of common salt. The other constituent is a body called sodium. It is found also in many compounds somewhat similar to salt, all of which are called chlorides. Salt is known as sodium chloride, while the next most abundant chloride is potassium chloride.

History. Chlorine was first prepared by the great Swedish chemist Scheele in 1774, and by a method which is still commonly employed for the purpose, viz., by the action of black oxide of manganese on hydrochloric acid. Scheele did not, however, recognize the true nature of the substance, and it remained for Humphrey Davy, in 1810, to supply this information and propose the name now given to the body.

Preparation. All methods of preparing chlorine depend on the decomposition of some of the chlorides. Usually we employ sodium chloride or hydrogen chloride, called also hydrochloric acid. The preparation by the use of hydrochloric acid will be illustrated first. This substance, as will appear later, is a compound of hydrogen and chlorine, and our problem is to separate one from the other. The next experiment will show how this can be done.

Experiment 61. In a flask holding 300 Cc. or more, take about 50 Gm. of manganese dioxide, the substance already used with potassium chlorate in the preparation of oxygen. Pour over the dioxide about 200 Cc. of commercial strong hydrochloric acid. Close the flask with a stopper having two perforations. Through one of these a funnel tube passes, the lower end dipping into the acid. A delivery tube passes out through the other perforation. This extends up about 6 or 8 Cm., and there is bent at right angles, the horizontal portion following having about the same length. To this, by means of a rubber connection, is joined a second bent glass tube, the longer limb of which has a length of about 20 Cm. The flask is supported on a sand-bath, as shown

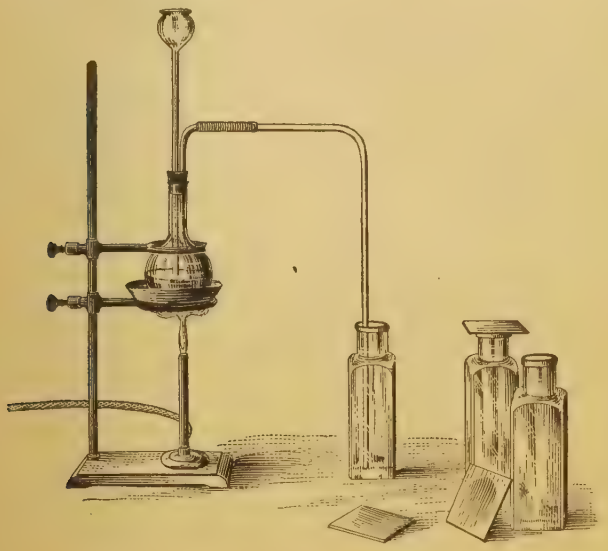

FIG. 12.

in the above figure, while the delivery tube extends down into an empty dry bottle of 200 to 300 Cc. capacity. When the flask is charged and properly mounted apply a gentle heat to the sand-bath. This hastens the action of the acid on the manganese dioxide. A greenish yellow gas soon fills the flask and passes over into the dry bottle. The delivery tube should enter the bottle through a piece of perforated cardboard, in order to prevent, as far as possible, the escape of the gas while the bottle is filling. As chlorine gas is much heavier than the air, it can be collected in this manner by displacement, the air being driven up out of

the bottle. When the bottle appears to be quite full of the gas remove it and put a second in its place. Collect four or five bottles of the gas. Each bottle as removed from the generator must be covered by a glass plate. After collecting the desired amount of the gas, replace the dry bottles by one containing water. Continue the application of heat and add more hydrochloric acid if necessary. Chlorine gas is somewhat soluble in water, and in this manner a solution is obtained which is used in a following experiment. *All experiments with chlorine must be performed in a fume closet.*

We have now several bottles of the gas, of which the greenish yellow color is characteristic. The odor also is marked and disagreeable in the extreme. The student must avoid, as far as possible, inhaling it, as it is exceedingly irritating to the air passages. In large amounts it is even very dangerous. For this reason the direction is given to carry out all experiments in a fume closet where there is sufficient draught to carry off any escaping gas. Having become aware of the more prominent features of the substance, the student may determine some of its properties by experiment.

Experiment 62. Chlorine is a strong bleaching agent, which may be shown as follows: Moisten a strip of colored calico in water and suspend it in one of the bottles of the gas, replacing the glass plate after introducing the fabric. In time the color fades through the destructive action of the chlorine. In the dry state the gas is practically without action, hence the direction given to moisten the calico. In the same bottle pour a little solution of indigo. If the bleaching of the calico has not removed all the chlorine the indigo color will be destroyed likewise.

This important property of the gas is utilized on the large scale in the wholesale bleaching of many articles. The action however is often destructive of the organic fiber itself.

Experiment 63. Chlorine has a marked affinity for many metals as well as for organic colors, and this may be illustrated by a very simple test. Remove the glass plate from one of the bottles, filled as above described, and put in its place a piece of wire gauze. Through this sift into the gas a little powdered antimony. The fine metal particles ignite as they fall in a shower through the gas and burn brightly, forming a chloride of antimony. Many other metals burn equally as well if they are taken in the form of fine wire or foil. Antimony in powder exposes a large surface to the action of the gas.

Chlorine was prepared above by decomposing its compound with hydrogen. It may readily be made to combine with hydrogen again, reproducing the acid. If equal volumes of the two gases be mixed in the dark and then exposed to the light, combustion often follows with a sharp explosion. The student is not advised to attempt this experiment as it is dangerous, unless carried out with certain precautions which need not be described here. The same affinity of hydrogen for chlorine may be shown in another manner without risk as will now be explained. Many substances are known which consist of hydrogen and carbon only. These bodies are called *hydrocarbons*. It has been found by experiment that chlorine gas is able to decompose a number of these substances, combining with the hydrogen to produce hydrochloric acid, while the carbon is set free as a fine black powder or soot. Among the hydrocarbons which exhibit this behavior, turpentine oil serves our purpose best, and will be employed therefore in our test.

Experiment 64. Pour some oil of turpentine in a test-tube, and in it immerse a strip of filter paper which has been twisted in the form of a taper. After withdrawing the paper press against it a second piece of dry filter paper, in order to absorb the excess of the oil taken up. Now remove the glass plate from a chlorine bottle and into it dip the taper, which in a few seconds darkens and finally burns with a very sooty flame, sending up a large volume of smoke. This consists of the liberated carbon, while hydrochloric acid vapors are formed, as can be shown by proper tests. For the success of this experiment the chlorine gas must be practically free from air, and the paper must not be wet but only moist from the action of the turpentine.

The same general behavior is shown by burning a small wax candle, or even a small jet of illuminating gas from a bent glass tube, in a bottle of the gas. Both the wax and illuminating gas contain hydrogen in combination with carbon. A combustion of either of these substances, begun in the air, continues in chlorine with a very sooty flame.

A small portion of the solution of chlorine water prepared above may be used for a bleaching test, but the larger portion should be preserved in a stoppered bottle, kept in a dark place, for several tests to follow.

Experiment 65. Prove that the chlorine water bleaches as does the gas, by immersing a piece of calico in it, or by pouring in some solution of indigo or litmus.

The method given above serves very well for making small quantities of chlorine for experimental purposes, but for the preparation of larger quantities the following process is much better.

The gas is generated in a large flask arranged as before, but from a mixture of salt, manganese dioxide and sulphuric acid. Mix about equal weights of the salt and the dioxide; pour this into the flask, and then through the funnel tube add gradually to the mixture about twice its weight of sulphuric acid, previously diluted with an equal weight of water. The flask is slowly heated on a sand-bath, and the gas is given off gradually.

If the gas is to be used for making pure chlorine water it should be led through a wash bottle first. In its simplest form this may consist of a wide mouth bottle holding about 250 Cc., closed with a stopper with two openings. Through one of these a tube from the generator passes and dips beneath the surface of water, which about half fills the bottle. A second tube passes up from the under surface of the stopper and bends over, to lead the gas to water or to collecting bottles, as desired. By this arrangement the gas is *washed* by bubbling through the water in the wash bottle. It loses small amounts of hydrochloric acid and other impurities carried over from the generator, as these are more soluble in water than chlorine is.

At 20° C. 1 volume of water dissolves 2.15 volumes of chlorine, and the solution so made can be kept a long time in a glass stoppered bottle in the dark. But exposed to light, gradual decomposition takes place, the hydrogen of the water combining with the chlorine to form hydrochloric acid, while the oxygen is liberated. In bright sunlight the action is comparatively rapid, as can very easily be shown by experiment.

Experiment 66. Fill a liter bottle with distilled water and pass chlorine gas into it to complete saturation. Close the bottle then with a stopper, so as to exclude all air, and invert it in a jar con-

taining strong chlorine water. Remove the stopper and stand the jar, with inverted bottle, in a window exposed to sunlight. In a short time gas bubbles will be seen to ascend through the liquid in the bottle. With average sunlight several days may elapse before the reaction is complete. The gas collected over the water in the bottle may now be tested. Insert the stopper in the bottle, bring it to the upright position, then withdraw the stopper and apply the usual test for oxygen by means of a glowing splinter. The reaction is distinct and characteristic. If the bottle is allowed to stand long enough in the light the green color and the odor of the chlorine disappear, while the sharp, hydrochloric acid odor can be noticed.

Other Methods of Preparation. Chlorine can be liberated by several other reactions, some of which have technical importance. One of these may be illustrated here by a brief experiment.

Experiment 67. Take a gram or two of powdered potassium dichromate in a test-tube and pour over it a few cubic centimeters of strong commercial hydrochloric acid. Apply heat. Decomposition of the hydrochloric acid soon takes place as shown by the appearance of greenish yellow fumes in the test-tube; that these consist of chlorine may be inferred from the color, odor and bleaching action easily determined. An explanation of this reaction will be given later.

A strong solution of hydrochloric acid may be decomposed by electricity in apparatus similar to that employed for the electrolysis of water. Several applications are made of this fact.

On the large scale chlorine is liberated in quantity and cheaply by what is known as the *Deacon* process, from the name of the discoverer. In this process a stream of hydrochloric acid gas is blown along with a stream of air through a series of heated tubes containing crushed brick impregnated with copper sulphate. The oxygen of the air takes the hydrogen of the acid and chlorine is left free, mixed with the nitrogen of the air. The crude chlorine so made is suitable for the production of bleaching powder and other products. Recently several electrolytic processes for the production of chlorine from salt have come into use.

General Tests for Chlorine. The common properties of chlorine are so marked that they afford easy means

of recognition. Like ozone and hydrogen peroxide, chlorine is able to decompose potassium iodide, and hence the so-called ozone test-paper, described in an earlier section, serves also as a chlorine test, when applied in moist condition to the gas supposed to contain or consist of chlorine. The methods by which chlorine may be recognized when mixed with other gases are described in Qualitative Analysis.

Physical Properties. As stated above, chlorine is somewhat soluble in water. One volume of water at 20° dissolves about 2.15 volumes of chlorine. With ice water it forms a crystalline compound. Under strong pressure gaseous chlorine may be condensed to a liquid having a specific gravity of 1.47 at 0°. This liquid is now an article of commerce. One liter of chlorine gas, at 0° and under a pressure of 760 Mm., weighs 3.2 grams.

Uses of Chlorine. While chlorine has many applications on the large scale, it has also some in the laboratory. The gas itself is frequently used and also the solution, or chlorine water. It was directed above to save some of this solution, and with it several experiments will be made, as explained a few pages in advance.

HYDROCHLORIC ACID.

History. This acid was known in crude form to the Arabian chemists and was made from salt and green vitriol in the 15th century. About the middle of the 17th century it was first made by a process like that employed to-day.

It has been already intimated that this substance may be formed by the direct union of chlorine with hydrogen, also by the action of chlorine on water in sunlight. It is usually prepared, however, by the decomposition of a *chloride* by means of sulphuric acid. The cheapest chloride known is *sodium chloride*, or common salt, and hence this substance is nearly always employed in the preparation. The reaction may be carried out very easily as a laboratory experiment, by a method now to be given.

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Experiment 68. Arrange apparatus as shown by the illustration.

The flask, to the left, on a sand-bath, has a capacity of about 500 Cc. It is charged with about 50 grams of common salt, and is closed by a stopper with two perforations, through one of which passes a funnel-tube leading nearly to the bottom of the flask. Through the other perforation a delivery tube passes, and this ends finally in a Woulfe bottle, half filled with water, but the delivery tube must not dip beneath the surface of the water here. Another tube leads from this first Woulfe bottle into a second, likewise half filled with water. In this case the tube dips beneath the surface of the water. From the second Woulfe bottle a tube leads to a flask of water. Each one of the Woulfe bottles

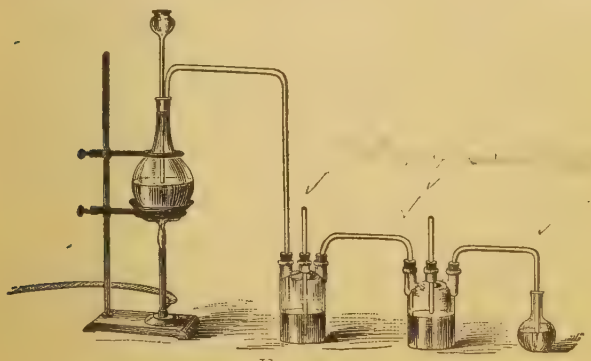


FIG. 13.

has three openings. Through one of these, in each case, a so-called safety tube passes and dips into the water. The object of these safety tubes is to provide for easy communication with the air in case the pressure of gas in the generating flask should suddenly diminish and the lower end of the funnel-tube should be closed by the materials around it. When the apparatus is in order, the flask containing the salt, as explained, pour in about 50 Cc. of strong sulphuric acid through the funnel-tube, a little at a time.

Immediately a very lively reaction begins. The mass in the flask froths and rises, while gas bubbles escape through the water in the second Woulfe bottle and the adjoining flask. This is air being expelled. The hydrochloric acid formed by the action of the sulphuric acid is now seen to enter the first Woulfe bottle and pass down from the end of the delivery tube to the water, and mix with it. The remarkable affinity of the water and gas is illustrated by this. After a time the flow of gas from the gen-

erator lessens and then heat should be applied to the sand-bath. At the beginning this is not necessary as the two substances react on each other in the cold. After a time the action in the flask ceases and no more gas passes over into Woulfe bottles. These are detached from the generator and their contents tested.

Experiment 69. Begin the tests by taking equal volumes of liquid, as a test-tube full, from the two Woulfe bottles and the small flask. Pour the contents of the test-tubes into three small clean beakers, and add to each a few drops of solution of silver nitrate. In the liquid from the first Woulfe bottle a heavy, curdy white precipitate forms, in that from the second the amount of precipitate is much less, while in the case of the liquid from the erd flask an opalescence only may result.

Experiment 70. Remove now three more equal portions as before, transfer them to clean beakers and add to each five drops of a weak alcoholic solution of *phenol-phthalein,* which may cause a faint opalescence of no consequence. Have at hand a dilute solution of sodium hydroxide (caustic soda) and add this gradually to the contents of each beaker, beginning with that from the small flask. One or two drops of sodium hydroxide solution may be sufficient to impart a red color to the liquid, and this indicates that the acid present has been fully neutralized by the solution added, which is an alkali. The phenol-phthalein is a substance which is turned bright red by alkaline solutions and hence it is employed here to show a change from acid to alkaline condition. It will be found that to neutralize the acid from the second Woulfe bottle more of the soda solution must be used, while for the liquid from the first Woulfe bottle a very large volume, relatively, of the alkali solution is necessary. It appears from this test that in the experiment most of the hydrochloric acid generated remains in the first Woulfe bottle.

The last two experiments show certain important properties of hydrochloric acid. It gives a precipitate with solution of silver nitrate, it neutralizes a strong alkali solution, and it is very soluble in water. We know this last to be true because both the silver and the alkali tests show that the most of the acid is in the water of the first bottle. That the acid is a gaseous body is indicated by the manner in which it is liberated in the beginning of the process when the sulphuric acid is first added to the salt. Without application of heat, it was seen that something passed over from the generating flask into the collecting bottle and this was evidently a gas.

It has been found by experiment that at 0° C. 1 vol-

ume of water absorbs very nearly 500 volumes of the gas. The common hydrochloric acid which we handle in liquid form is merely an aqueous solution of the gas, containing from 25 to 40 per cent by weight of the real acid. For many purposes the strong acid is diluted, before use, with more water. With about 10 cubic centimeters of the strong acid solution in the first Woulfe bottle make the following experiment.

Experiment 71. Transfer the acid to a small beaker and add a few drops of the phenol-phthalein indicator. Then pour in very gradually, as before, some caustic soda solution until a red color just appears. Now, by means of a glass rod, add a drop or two more of the acid, or sufficient to discharge the color. This yields a very nearly neutral solution, the acid being only slightly in excess. Pour the liquid into a clean porcelain evaporating dish and boil it down to dryness. If during the evaporation the red color returns it shows that insufficient acid has been added and a drop or two more may be mixed with the liquid. When the evaporation is complete heat strongly a few minutes longer, allow to cool and observe the taste. We have here common salt, similar to that decomposed in the large flask in the reaction with sulphuric acid.

In this series of experiments we have illustrations of some very important chemical reactions. In the making of hydrochloric acid we decompose salt, which is a compound body, and secure two new substances. One of these is the gas hydrochloric acid which distills over, while the other is a solid substance, left in the generating flask, and is known as sodium sulphate. When it is seen that in neutralizing the hydrochloric acid with the soda solution we reproduce salt it becomes evident that the soda adds in the last experiment that which the sulphuric acid must have separated in the first. Hydrochloric acid on the large scale is often produced as a by-product in the manufacture of alkali from sodium or potassium chloride, as will be explained later. Sodium sulphate and potassium sulphate, formed as above illustrated, are converted into sodium and potassium carbonates.

Experiment shows that this acid is very active in the solution or decomposition of many bodies. It dissolves iron, zinc and several other metals forming chlorides, its hydrogen being liberated. It dissolves marble and other

carbonates with liberation of carbonic acid gas and formation of chlorides.

Physical Properties. Hydrochloric acid can be condensed to a liquid under considerable pressure and in this form has a specific gravity of 1.27. A liter of the gas, under standard conditions, weighs 1.643 grams. As mentioned, the gas is extremely soluble in water, it being possible to prepare at a low temperature a solution which contains 45 per cent by weight of the acid. This solution is not stable at higher temperatures. A solution of 42 per cent strength can be made to keep. Our strongest commercial acid has usually a strength of about 40 per cent. The stronger grades fume when exposed to the air because of a combination of the real acid with the moisture present.

Uses. Hydrochloric acid is employed for numerous purposes in the chemical laboratory and in technical operations on the large scale. Much of the crude by-product, mentioned above, is employed in the manufacture of bleaching powder.

ELEMENTS AND COMPOUNDS.

Enough work has been done thus far by the student to make him acquainted with certain fundamental differences between bodies. Oxygen has been prepared by several methods, and it was found that it could be readily combined with several other substances. Hydrogen and chlorine likewise were secured in the free pure condition and in turn were united with other bodies to form new substances. Nowhere has anything been said about the decomposition or breaking up of oxygen, hydrogen and chlorine themselves. The question might naturally occur to the student, why, in experimenting with these three bodies, has no experiment been given in which they in turn should be decomposed.

The fact is that up to the present time no means have been found by which these three substances, and many others to be mentioned later, can be resolved into any-

thing simpler. The numerous and powerful methods of decomposition known to chemists have been applied in vain to the splitting of these bodies, and hence they have come to be regarded as the real *elements* of the material world. They cannot be decomposed, it appears, but they can combine to form other substances. The new substances are called compounds, and of these we have already had in our work many illustrations. Water, common salt, hydrochloric acid, sulphuric acid, mercuric oxide, potassium chlorate, carbon dioxide, hydrogen dioxide and other bodies produced or used were shown by experiment to be compound in their nature. In all these cases the existence of at least two elements was shown or could be inferred with certainty from the experimental results.

There appear to be about seventy-eight of these elementary substances, while the number of compound bodies known is enormously large. That hydrogen, oxygen, chlorine and the other so-called elements are really elementary, that they can never be decomposed, yielding other substances, we cannot safely affirm; indeed, water and many other compound bodies were once looked upon as elements. But this much may be safely said, that with the means now at our command, we cannot decompose them, and, therefore, for all practical purposes they must be looked upon as elementary.

ATOMS AND MOLECULES.

A systematic or scientific study of chemical phenomena began toward the end of the eighteenth century, and, as already pointed out, the conditions under which many of the elements combine were soon recognized. It was found, among other things, that the power of combination is limited; in other words that the elements can be made to unite, as a rule, in certain proportions only. Several cases were known in which metals combined with oxygen in more than one proportion, but even the crude analyses of the time were sufficient to show that in the more highly oxidized bodies the amount of oxygen present is a multi-

ple of that in the lower. In the two oxides of nitrogen known at the beginning of the nineteenth century, it was found that one contains just twice as much oxygen as the second. The same relation was pointed out for the two compounds of carbon and oxygen known, and John Dalton found that in two compounds of carbon and hydrogen known the ratio of the weight of the carbon to that of the hydrogen is just twice as great in one case as in the other. These observed facts naturally caused much speculation among chemists, but Dalton was the first to propose a satisfactory hypothesis to account for them.

From the earliest times philosophers were familiar with the idea that matter exists ultimately in the form of minute indivisible particles called atoms, and although this view was not regarded in general as of fruitful importance, Dalton was able to develop it further and make finally much of it. After applying the conception to the explanation of several purely physical phenomena, he employed it to account for the formation of chemical compounds by the union of minute particles or atoms of constant weight. According to him an atom of hydrogen unites with an atom of oxygen to form water; an atom of hydrogen with an atom of nitrogen to form ammonia; an atom of hydrogen with an atom of carbon to form ethylene. A contemporary of Dalton, Thomson, explaining the views of the former, uses this language:

"One atom of a body, *a*, unites with one atom of a body, *b*, or with two atoms of it, or with three, four, etc., atoms of it. The union of one atom of *a* with one of *b* produces one compound, the union of one atom of *a* with two atoms of *b* produces another compound, and so on."

"We have no means of demonstrating the number of atoms which unite together in this manner in every compound; we must, therefore, have recourse to conjecture. If two bodies unite only in one proportion, it is reasonable to conclude that they unite atom to atom. Hence it is most likely that water is composed of one atom of oxygen and one atom of hydrogen; oxide of silver, of one atom of silver and one atom of oxygen; and oxide of zinc, of one atom of zinc and one atom of oxygen."

"If we know the number of atoms of which a body is combined, and the proportion of the constituents, there is no difficulty in determining the proportional weight of the atoms of which it is composed. Thus, if water be composed of one atom of oxygen and one atom of hydrogen, and if the weight of the oxygen in water is to that of the hydrogen as 7½ to 1, then it follows that the weight of an atom of oxygen is to that of an atom of hydrogen as 7½ to 1."

The above quotations express clearly Dalton's notion of the combination of atoms to form larger groups, which we now call molecules. Because of lack of sufficient experimental data he was led to assume that compounds formed by the union of atoms are in many cases simpler than we now have reason to consider them, but this is a detail which does not detract from the theory. Dalton recognized that the weights of these minute atoms must be exceedingly small and beyond the reach of practical determination. He therefore proposed a new system of weights, the weight of the atom of hydrogen being taken as the standard and called unity. The weights belonging to this system are commonly called *the atomic weights,* and one method of arriving at their value is suggested in the above quotation; other methods will be pointed out later.

Since the time of Dalton many new elements have been discovered and exact analytical methods have been perfected by which the weights of their ultimate atoms on the hydrogen scale may be readily found. For certain practical reasons Berzelius, a contemporary of Dalton, suggested the atom of oxygen as the standard and proposed to call its weight arbitrarily 100. This suggestion did not meet with general favor. To-day, however, many chemists agree with Berzelius in his reasons for preferring the atom of oxygen, rather than the atom of hydrogen, as the standard, but place its weight at 16, which is very nearly its true weight on the hydrogen scale. The table given below contains a list of the elements with their atomic weights on the hydrogen scale and on the oxygen scale. This table is the compilation of the so-

called International Committee on Atomic Weights, and is now commonly followed among chemists. In the fifth column of the table are given some approximate values obtained by rounding off the numbers of the fourth column. These approximate values are convenient and sufficiently accurate for the calculation of problems to be given later, and also for the illustrations which follow. The first column contains the name of the element and the second column the symbol by which it is represented.

Table of Atomic Weights.

Name.	Symbol.	H = 1.	O = 16.	Approx.
Aluminum	Al	26.9	27.1	27.1
Antimony	Sb	119.3	120.2	120.2
Argon	Ar	39.6	39.9	40.0
Arsenic	As	74.4	75.0	75.0
Barium	Ba	136.4	137.4	137.4
Bismuth	Bi	206.9	208.5	208.5
Boron	B	10.9	11.0	11.0
Bromine	Br	79.36	79.96	80.0
Cadmium	Cd	111.6	112.4	112.4
Cæsium	Cs	131.9	132.9	—
Calcium	Ca	39.7	40.1	40 1
Carbon	C	11.91	12.00	12.0
Cerium	Ce	139.2	140.2	—
Chlorine	Cl	35.18	35.45	35.5
Chromium	Cr	51.7	52.1	52.1
Cobalt	Co	58.55	59.0	59.0
Columbium	Cb	93.3	94.0	—
Copper	Cu	63.1	63.60	63.6
Erbium	Er	164.8	166.0	—
Fluorine	F	18.9	19.0	19.0
Gadolinium	Gd	154.8	156.00	—
Gallium	Ga	69.5	70.0	—
Germanium	Ge	72.0	72.5	—
Glucinum	Gl	9.0	9.1	—
Gold	Au	195.7	197.2	197.2
Helium	He	4	4	4.0
Hydrogen	H	1.00	1.008	1.0
Indium	In	114.1	115.0	—
Iodine	I	126.01	126.97	127.0
Iridium	Ir	191.5	193.0	—
Iron	Fe	55.5	55.9	56.0
Krypton	Kr	81.1	81.8	—
Lanthanum	La	137.9	138.9	—

Name.	Symbol.	H = 1.	O = 16.	Approx.
Lead	Pb	205.35	206.9	206.9
Lithium	Li	6.98	7.03	7.0
Magnesium	Mg	24.18	24.36	24.4
Manganese	Mn	54.6	55.0	55.0
Mercury	Hg	198.5	200.00	200.0
Molybdenum	Mo	95.3	96.0	96.0
Neodymium	Nd	142.5	143.60	—
Neon	Ne	19.9	20	—
Nickel	Ni	58.3	58.7	58.7
Nitrogen	N	13.93	14.04	14.0
Osmium	Os	189.6	191.0	—
Oxygen	O	15.88	16.00	16.0
Palladium	Pd	105.7	106.5	
Phosphorus	P	30.77	31.00	31.0
Platinum	Pt	193.3	194.8	194.8
Potassium	K	38.85	39.15	39.1
Praseodymium	Pr	139.4	140.5	
Radium	Ra	223.3	225	
Rhodium	Rh	102.2	103.0	
Rubidium	Rb	84.8	85.5	
Ruthenium	Ru	100.9	101.7	
Samarium	Sm	149.2	150.3	
Scandium	Sc	43.8	44.1	
Selenium	Se	78.6	79.2	79.2
Silicon	Si	28.2	28.4	28.4
Silver	Ag	107.11	107.93	107.9
Sodium	Na	22.88	23.05	23.0
Strontium	Sr	86.96	87.6	87.6
Sulphur	S	31.82	32.06	32.1
Tantalum	Ta	181.6	183.0	
Tellurium	Te	126.6	127.6	127.6
Terbium	Tb	158.8	160.0	
Thallium	Tl	202.60	204.1	
Thorium	Th	230.8	232.5	
Thulium	Tm	169.7	171.0	
Tin	Sn	118.1	119.0	119.0
Titanium	Ti	47.7	48.1	
Tungsten	W	182.6	184.00	
Uranium	U	236.7	258.5	258.5
Vanadium	V	50.8	51.2	
Xenon	Xe	127	128	
Ytterbium	Yb	171.7	173	
Yttrium	Yt	88.3	89	
Zinc	Zn	64.9	65.4	65.4
Zirconium	Zr	89.9	90.6	

Use of Symbols. We have reached a point now in our work where very great help is derived from the use of symbols representing the substances dealt with, and the student is advised to learn those of the important elements in the table.

The first use of a symbol is as an abbreviation of the name of a substance dealt with. Thus, we use H as standing for or representing hydrogen, O as representing oxygen, S as representing sulphur, and so on. Employed in this manner, we use the symbol merely to save time or space in writing. But there is a second and much more important application of these letters as representing something. H stands for the *smallest weight* of the element hydrogen, which can exist in any compound or take part in any reaction, O for the smallest weight of oxygen, S for the smallest weight of sulphur combining or existing in the same manner. According to the definition given above these symbols, therefore, represent weights of the several substances corresponding to the atomic weights. In all of our calculations O stands for 16 parts of oxygen, H for 1 part of hydrogen, Cl for 35.5 parts of chlorine, Na for 23 parts of sodium, and so on.

Molecules and Molecular Weight. The atoms of the elements mentioned above combine among themselves to form groups called molecules. Two atoms of hydrogen unite with one atom of oxygen to form a molecule of water; an atom of oxygen forms with an atom of mercury a molecule of mercuric oxide; two atoms of carbon, six atoms of hydrogen and one atom of oxygen in combination constitute a molecule of alcohol. We represent molecules by uniting the symbols of their component atoms. Thus, for the above illustrations: H_2O, HgO, C_2H_6O.

We call this combination of symbols a formula. A *symbol* is, therefore, arbitrarily taken to represent an atom, while a *formula* represents a molecule.

We may now apply some of these facts in explanation of experiments in the preceding chapters. In our experiment on the decomposition of mercuric oxide, with libera-

tion of oxygen, we may represent what takes place by this equation:

$$\underset{\text{oxide}}{\overset{\text{Mercuric}}{HgO}} = \underset{\text{Mercury}}{Hg} + \underset{\text{Oxygen}}{O}$$

This equation tells us that 216 parts of the compound, mercuric oxide, yield when heated 200 parts of the element mercury and 16 parts of the element oxygen. In the decomposition of potassium chlorate we have a more complex case. This is a combination of potassium, oxygen and chlorine from which the oxygen may be readily separated by heat. A study of the compound, potassium chlorate, shows that it contains its elements in these proportions by weight: oxygen, 48 parts; chlorine, 35.5 parts; potassium, 39.1 parts. The atomic weights or combining weights are represented here, three times for oxygen, once for chlorine and once for potassium. We therefore write as the *formula* of our compound, $KClO_3$. When we decompose this we find that all of the oxygen is given off and that we have a solid substance left which contains potassium and chlorine in the proportions in which they were found in the original compound. We therefore write this equation, *as expressing the results of our experiment:*

$$\underset{\text{chlorate}}{\overset{\text{Potassium}}{KClO_3}} = \underset{\text{chloride}}{\overset{\text{Potassium}}{KCl}} + \underset{\text{Oxygen}}{O_3}$$

The student must early recognize this fact, that a chemical equation is always written to show, in compact form, what experiment proves has taken place or must take place under proper conditions. Chemical symbols cannot be combined at random, we cannot perform operations on them as we do with algebraic symbols, but when we write them on the left hand side of our equality sign we simply name the substance or substances on which some experiment is to be performed. *After the experiment* we are able to complete the equation, and then we write down on the other side of the equality sign what has taken place.

The above equation shows, correctly, only the relations by weight between the substance taken and the products. Careful experiments have made it plain that the reaction really takes place in two stages, as represented by the following equations:

$$2KClO_3 = KClO_4 + KCl + O_2$$

Potassium chlorate yields at first a substance known as potassium perchlorate with potassium chloride and a relatively small amount of oxygen, in fact just one-third, by weight, of that in the original compound. At a high temperature the potassium perchlorate, represented by the formula $KClO_4$, breaks up into more potassium chloride and oxygen, thus,

$$KClO_4 = KCl + O_4$$

Combining the two equations we can therefore write:

$$2KClO_3 = KCl + KCl + O_2 + O_4,$$

or better,

$$2KClO_3 = 2KCl + 3O_2$$

Why we write $3O_2$ instead of O_6 is a question which cannot be satisfactorily answered at this point, but will be taken up later in consideration of other experimental results; but another simple matter in connection with the method of writing equations must be explained here. The student observes that numerals are employed in two positions in these equations. Large figures are written before the formulas of compounds, while small figures in several cases seem to be to the right and a little below certain symbols. This is a purely conventional arrangement, and the meaning conveyed could be just as well expressed in some other manner. It has been agreed by chemists to consider the large numerals as multiplying the whole compound which follows, while the small figures are taken as referring only to the symbol of the element immediately preceding. Thus, in $2KClO_3$ we have twice the whole

group, while the small 3 indicates that we have in each group the combining weight of oxygen taken three times. The effect of the large numerals, however, is not carried beyond a sign of addition or subtraction. In the equation,

$$2KNO_3 + H_2SO_4 = K_2SO_4 + 2HNO_3,$$

the large 2 at the beginning refers only to the KNO_3, and not to H_2SO_4.

We may now express, by the use of symbols, the reactions which took place in some of the experiments on oxygen. We have

$$\begin{array}{rcl} C + O_2 & = & CO_2 \\ \text{Carbon} + \text{Oxygen} & = & \text{Carbon dioxide} \end{array}$$

$$\begin{array}{rcl} S + O_2 & = & SO_2 \\ \text{Sulphur} + \text{Oxygen} & = & \text{Sulphur dioxide} \end{array}$$

$$\begin{array}{rcl} P_4 + 5O_2 & = & 2P_2O_5 \\ \text{Phosphorus} + \text{Oxygen} & = & \text{Phosphorus pentoxide} \end{array}$$

In the first case we have the union of 12 parts of carbon with 32 parts of oxygen. In the second case 32.1 parts of sulphur combine with 32 parts of oxygen, while in the third case 124 (4×31) parts of phosphorus combine with 160 (5×32) parts of oxygen.

The combining weight of zinc has been found to be 65.4, and we find that 65.4 parts of zinc act on 98.1 parts of sulphuric acid, liberating 2 parts of hydrogen. We therefore write the equation,

$$\begin{array}{rcl} Zn + H_2SO_4 & = & ZnSO_4 + H_2 \\ \text{Zinc} + \text{Sulphuric acid} & = & \text{Zinc sulphate} + \text{Hydrogen} \end{array}$$

This equation, like all the others, is intended to express the results of experiments. We find that sulphuric acid is composed of hydrogen, oxygen and sulphur in certain proportions shown by the formula H_2SO_4, and that at the end of the experiment we have in solution a compound which contains, in place of hydrogen, zinc combined with oxygen and sulphur, in the proportions shown by the formula $ZnSO_4$, and which is known as zinc sulphate.

By the symbol H we represent 1 combining weight of hydrogen, and by H_2 we represent two such weights. By our equation, therefore, we express this fact, that in the solution of 65.4 parts of zinc we liberate 2 parts by weight of hydrogen. To generate 2 grams of hydrogen gas by this method we must dissolve 65.4 grams of the metal zinc.

It has been already mentioned that we may use iron instead of zinc for the generation of the hydrogen gas. In this case we find that 56 parts of iron produce the same amount of hydrogen that we obtain from the 65.4 parts of zinc. The 56 represents, in fact, the combining weight of iron, and we may write as expressing the last reaction,

$$\begin{array}{ccccccc} Fe & + & H_2SO_4 & = & FeSO_4 & + & H_2 \\ \text{Iron} & + & \text{Sulphuric acid} & = & \text{Ferrous sulphate} & + & \text{Hydrogen} \\ 56 & + & 98.1 & = & 152.1 & + & 2 \end{array}$$

The sum of the weights on the left hand side of the equation is equal to the sum on the right. There is neither a gain nor loss of matter, but merely a rearrangement of elements in the compounds. It appears from these illustrations that zinc and iron have the power of *displacing* the hydrogen in the acid used. Had we used hydrochloric acid instead of sulphuric exactly the same behavior would have been observed. Hydrogen would have been displaced in quite the same manner, and 2 parts by weight for 65.4 parts of zinc, or 56 parts of iron dissolved. In general, it may be said that zinc and iron displace hydrogen in many bodies called acids, and always in the proportions given.

We come now to a consideration of the reactions by which chlorine and hydrochloric acid were produced, and here again we deal with the results of exact experiments. It has been found that sulphuric acid is able to decompose sodium chloride, or common salt, in a manner illustrated by the following equation:

$$\begin{array}{ccccccc} H_2SO_4 & + & 2NaCl & = & Na_2SO_4 & + & 2HCl \\ \text{Sulphuric acid} & + & \text{Sodium chloride} & = & \text{Sodium sulphate} & + & \text{Hydrochloric acid} \\ 98.1 & + & 117 & = & 142.1 & + & 73 \end{array}$$

Experiment actually shows us that for an amount of sulphuric acid represented by the sum of the combining weights of its elements, that is for 98.1 parts by weight, we require 117 parts of salt, that is, twice the sum of the combining weights of the sodium and chlorine.

When we employ the pure materials in exactly these proportions, and aid their action on each other by heat, we find at the end of our experiment that we have neither sulphuric acid nor salt, but two new substances, one of which is the hydrochloric acid, which we collect in water, and the other a white solid substance which remains in the decomposing vessel, and which we call sodium sulphate. There are no other products in the reaction. We call this a reaction of *double decomposition*, inasmuch as we start with two compound bodies which react on each other to form two *new* compound bodies. We can illustrate this double decomposition by a diagram, as follows:

Before the reaction, one compound body is made up of the parts A and B, and the other compound body of the parts C and D. But after the decomposition we have a new compound body, with A and D as its parts, and another with C and B. The reaction between salt and sulphuric acid is a typical one of double decomposition and well illustrates many which are to follow.

From our hydrochloric acid, as made above, we separate the chlorine by another process described. This is somewhat more complex, but its exact nature may be readily illustrated as follows:

$$\underset{\text{Manganese dioxide}}{MnO_2} + \underset{\text{Hydrochloric acid}}{4HCl} = \underset{\text{Manganese chloride}}{MnCl_2} + \underset{\text{Water}}{2H_2O} + \underset{\text{Chlorine}}{Cl_2}$$

$$87 + 146 = 126 + 36 + 71$$

The manganese dioxide in the above is made up of the combining weight of manganese plus twice that of oxy-

gen. Now experiment shows that to decompose this completely we need of hydrochloric acid four times the sum of the combining weights of hydrogen and chlorine. Less would not be sufficient to complete the decomposition of the manganese dioxide. The experiment may be performed in such a manner as to show that water is liberated, and exactly how much. For the amount of manganese dioxide assumed to be taken we find of water just twice the sum of the combining weights of hydrogen and oxygen, the weights taken or obtained being expressed in any convenient standard, as in grams. The chlorine liberated is just half of that contained in the original hydrochloric acid used, which fact is expressed also in the equation.

When chlorine is liberated by the action of salt, sulphuric acid and manganese dioxide on each other, the whole of that element in the salt may be obtained. The reaction takes place in two stages possibly, the first involving the formation of hydrochloric acid and the second its decomposition. The following equation shows the quantitative relations existing between the compounds taken and obtained.

$$\begin{array}{rcl} MnO_2 + 2NaCl + 2H_2SO_4 = & & \\ 87 \quad + \quad 117 \quad + \quad 196.2 \quad = & & \\ & & MnSO_4 + Na_2SO_4 + 2H_2O + Cl_2 \\ & & 151.1 \quad + \quad 142.1 \quad + \quad 36 \quad + 71 \end{array}$$

From the above it appears that the manganese dioxide used, and chlorine obtained stand to each other in the relation of 87 to 71. As both weights are referred to the same basis or standard, the proportion must hold good if we refer them to a new standard. If we take the gram as our unit it is true that 87 grams of manganese dioxide must be used for the liberation of 71 grams of chlorine, and if we weigh in pounds or tons the same ratio must still exist. It is easy, therefore, to tell how much manganese dioxide must be used to liberate any given quantity, as 100 grams, of chlorine. It is evident that the cor-

rect answer must be given by the following proportion:

$$87 : 71 :: x : 100$$
$$x = 122.5 \text{ grams}$$

To find the amount of salt required we make another proportion:

$$117 : 71 :: x : 100$$
$$x = 164.8 \text{ grams}$$

A third proportion shows the amount of sulphuric acid necessary for the formation of the 100 grams of chlorine:

$$196.2 : 71 :: x : 100$$
$$x = 276.3 \text{ grams}$$

Aided by the above explanations the student should now be able to understand what follows. From this point on all important reactions will be represented by equations, and these should be thoroughly studied. The student should keep in mind, however, that equations are not drawn from the imagination, but represent, properly, the results of experiments. He should practice writing them as an aid to memorizing important reactions, and especially because of their value in the solution of even the simplest chemical problems, as illustrated by the examples given above.

In the present chapter no attempt will be made to explain methods by which the atomic weights are found. In one to follow, however, after the student has become more familiar with chemical facts, something on this topic will be given.

CHAPTER IV.

COMPOUNDS OF CHLORINE WITH OXYGEN. BROMINE, IODINE, FLUORINE AND THEIR COMPOUNDS.

In the last chapter the element chlorine and its compound with hydrogen have been described. In this chapter a few other important combinations must be referred to.

OXIDES AND ACIDS OF CHLORINE.

Three compounds of chlorine with oxygen are known, but they cannot be formed by direct union.

Chlorine Monoxide and Hypochlorites. The first one is called chlorine monoxide, and is represented by the formula Cl_2O. It is a yellowish brown gas with an odor suggesting chlorine, and may be made by passing dry chlorine over the red oxide of mercury, freshly precipitated and dried, and contained in a glass tube. This equation expresses the combination:

$$HgO + 2Cl_2 = HgCl_2 + Cl_2O$$

The gas can be easily condensed to a liquid, but this is not stable. It is very soluble in water, forming a new acid, called hypochlorous acid:

$$Cl_2O + H_2O = 2HOCl$$

The acid solution is not stable; if the gas is led into an alkali solution, however, an important body called a *hypochlorite* is formed:

$$Cl_2O + 2KOH = 2KOCl + H_2O$$

Some of the hypochlorites are well known and useful substances. Calcium hypochlorite is the active constituent of *bleaching powder*. Sodium and potassium hypochlorites are used in the laboratory and in medicine. These hypochlorites are easily decomposed by hydrochloric or sulphuric acid with liberation of chlorine. Practical application is made of this in bleaching by bleaching powder, which is illustrated by the following experiment:

Experiment 72. Pour some dilute sulphuric acid over a few grams of bleaching powder in the bottom of a large beaker which then cover with a piece of glass or a card. Observe that greenish yellow fumes soon collect in the beaker. Moisten now a piece of bright calico, as already described, and hang it in the beaker of gas. The calico will fade as before.

The manufacture of bleaching powder will be referred to later. It is made by passing chlorine gas over slaked lime, and is essentially a mixture of calcium hypochlorite, CaO_2Cl_2, and calcium chloride, $CaCl_2$, in about equal proportions.

Chlorine Dioxide. This is a heavy dark yellow gas usually made by the decomposition of potassium chlorate by sulphuric acid. Chloric acid, $HClO_3$, is formed first and this decomposes on slight warming.

$$3HClO_3 = HClO_4 + 2ClO_2 + H_2O$$

The gas can be condensed to a liquid at a low temperature. It is not stable, often decomposing with explosive violence. It dissolves rather readily in water but does not form a new acid.

Chlorine Trioxide. This is a greenish yellow gas having the composition Cl_2O_3 and is made by several processes depending on the reduction of chloric acid, $HClO_3$. It is decomposed by warm water forming a mixture of hydrochloric and chloric acids, and with cold water yields chlorous acid, as below.

Chlorous Acid, $HClO_2$, is not known in the pure state, but certain salts, called chlorites, are known and these correspond to the acid.

Solutions of chlorous acid result when the trioxide is dissolved in water:

$$Cl_2O_3 + H_2O = 2HClO_2$$

Chloric Acid. This is the best known of the oxygen acids of chlorine and may be prepared by decomposing barium chlorate by means of sulphuric acid:

$$Ba(ClO_3)_2 + H_2SO_4 = 2HClO_3 + BaSO_4$$

As barium sulphate, $BaSO_4$, is a very insoluble precipitate it is easy to obtain a pure solution of the chloric acid by pouring off the supernatant liquid. The concentrated acid is a strong oxidizing agent, has a pungent odor and decomposes readily when heated, yielding a new acid known as perchloric acid, $HClO_4$, along with oxygen and chlorine. Corresponding to chloric acid, we have the well-known salts called chlorates, of which potassium chlorate, $KClO_3$, is the best illustration. The chlorates are all soluble in water and decompose when heated, yielding oxygen. The decomposition takes place in two stages, however; in the first perchlorate is formed:

$$2KClO_3 = KClO_4 + KCl + O_2$$

In the second stage of the reaction the perchlorate is decomposed, yielding more oxygen and chloride.

Perchloric Acid. As potassium perchlorate is but slightly soluble in water, advantage is taken of the above reaction in preparing perchloric acid, $HClO_4$. When the chlorate is heated until the evolution of oxygen begins the first stage of the reaction may be considered as completed, practically. If the mass is now cooled, powdered and extracted with water the perchlorate is left while the chloride goes into solution. This perchlorate distilled with strong sulphuric acid yields perchloric acid, which is a heavy, volatile liquid having a great affinity for water. It is a powerful oxidizing agent and decomposes immediately when brought in contact with most organic sub-

stances. The perchlorates are all soluble in water and they differ from the chlorates in not being decomposed by hydrochloric acid.

It appears from the foregoing that we have four chlorine acids containing oxygen. The names and formulas of these are:

Hypochlorous acid, $HClO$,
Chlorous acid, $HClO_2$,
Chloric acid, $HClO_3$,
Perchloric acid, $HClO_4$

It will be observed that the names differ through certain prefixes and terminations and it will be seen later that the same are used in the designations of all other acids.

OTHER CHLORINE COMPOUNDS.

Chlorine combines indirectly with nitrogen to form a very explosive substance known as nitrogen chloride. It forms a number of important combinations with carbon and with carbon and hydrogen, to be mentioned later. A very important compound with oxygen and nitrogen will be described in the next chapter.

BROMINE.

Occurrence. Bromine is an important element which never occurs free in nature. It is found in several bromides in spring waters, and to a slight extent in sea water.

History. Bromine was discovered in 1826 by Balard in the mother liquor left after crystallization of salt from evaporated sea water. The discoverer was able to show the important analogies existing between this element and chlorine and iodine.

Preparation. Much of our bromine is obtained from the residues left on crystallizing salt from concentrated brine of certain salt springs. The bromine is left in these mother liquors in the form of bromides, which are more soluble than the common salt, and may be liberated by several reactions, of which two illustrations will be given,

Large quantities of bromine are produced at the Michigan salt wells and also from the salt deposits of Stassfurt, Germany. The production in the United States in 1904 was about 900,000 pounds.

Experiment 73. Dissolve a small crystal of sodium or potassium bromide in water in a test-tube, and add gradually, a drop at a time, some chlorine water. Use for this purpose the chlorine water saved from a former experiment. When the first drop of chlorine water mixes with the solution of bromide it produces a reddish-yellow color which deepens to red as more of the reagent is added. If the bromide solution is weak and the chlorine water strong, the red color will finally disappear by continued addition of the latter. The chlorine water decomposes the bromide, liberating bromine.

In the above experiment we have illustrations of several important points. First, of the liberation of free bromine. Potassium bromide is a combination of bromine with potassium, which we represent by the formula KBr. Sodium bromide is represented by NaBr. Assuming that we are dealing with the former we express the whole reaction by this equation:

$$\begin{array}{l} KBr + Cl = KCl + Br \\ 119.1 + 35.5 = 74.60 + 80 \end{array}$$

The equation shows just what an exact quantitative experiment would have revealed to us, viz., that 35.5 parts by weight of chlorine are required to completely decompose 119.1 parts of potassium bromide with liberation of 80 parts of bromine. The weight of chlorine taken and that of bromine obtained are chemically equivalent, but, as the result shows, the chlorine is able to displace the bromine. We are no more able to give an exact reason for this displacement than we are to assign a reason for other chemical decompositions already illustrated. But we are accustomed to say that the chlorine has a greater affinity for the potassium than the bromine has and is therefore able to drive it out from its combination. Of the real nature of this chemical affinity we know but little.

The above experiment illustrates the marked activity of chlorine in another manner. It was shown that a

great excess of the chlorine water discharged the color of the free bromine. This loss of color is due to two causes. First, to the combination of the excess of chlorine with the bromine liberated, forming bromine chloride, and second, to the *oxidation* of some of the bromine to bromic acid, in presence of water, which is illustrated by this equation:

$$Br + 3H_2O + 5Cl = 5HCl + HBrO_3$$

Hydrochloric and bromic acids result.

Bromine can be readily liberated from bromides by a reaction analogous to that employed for the preparation of chlorine from chlorides, that is, by the use of sulphuric acid and manganese dioxide. The following experiment will illustrate this:

Experiment 74. In a 300 Cc. flask mix about 2 Gm. of powdered potassium bromide with 4 or 5 Gm. of commercial powdered manganese dioxide. Add a little water and shake until the mixture becomes uniformly distributed. Then add 50 Cc. of dilute sulphuric acid and close the flask with a stopper through which passes a long delivery tube bent down to dip into a small flask or beaker of cold water. The flask with the above described mixture must stand on a sand-bath or wire gauze, which is then heated by a lamp. Red vapors are generated in the flask which distill over and dissolve in the water in the small receiving flask or beaker. Continue the application of heat as long as these red vapors are evolved. Then remove the receiving flask and withdraw the lamp from the other flask.

The reaction which takes place here is illustrated by this equation:

$$2KBr + MnO_2 + 2H_2SO_4 = Br_2 + MnSO_4 + K_2SO_4 + 2H_2O$$

This is seen to be similar to the chlorine reaction. A very large excess of manganese dioxide is taken in the experiment, in order to secure the complete decomposition of the bromide without liberation of hydrobromic acid.

On the large scale this process is applied to the manufacture of bromine from the mother liquors of salt works.

As these liquors contain much chloride, chlorine is first liberated and this serves to free the bromine. Some bromine chloride is always produced in the operation, but this is more volatile than the bromine and can be separated by distillation.

In the experiment just described, bromine was collected in water. It is somewhat soluble in water, as shown by the fact that at first all that distilled over went into solution. Before the end of the experiment, however, unless too much water was taken, a part of the bromine settles out as a dark red drop. Use this aqueous solution of bromine for tests as follows.

Experiment 75. Bromine bleaches as does chlorine, but with less activity. Test this by use of colored calico, and also with solutions of organic coloring matters, litmus and cochineal, for instance.

Bromine is readily soluble in chloroform, carbon disulphide, ether and other liquids, and may be withdrawn from aqueous solution by them.

Experiment 76. Pour some of the bromine water, made above, into a test-tube, and add about one-tenth its volume of carbon disulphide. Close the tube with a cork and shake thoroughly. On standing, the disulphide speedily collects at the bottom of the tube, and it will be seen that it is highly colored by the absorbed bromine, while the water above is much lighter colored than before, or it may be even colorless. This beautiful reaction is employed in the detection of small traces of bromides in spring water, the bromine being first liberated by means of a small amount of chlorine.

Physical Properties. Bromine boils at 63°, and freezes about —7°. At 0° it has a specific gravity of 3.18. At 15° it dissolves in 33 parts of water.

Uses. Bromine is employed in the preparation of bromides, several of which are used in medicine. It is used also in making certain reagents employed in laboratories and in making a number of valuable organic preparations.

BROMINE AND HYDROGEN.

Under certain conditions these two elements may be directly united, but not as readily as is the case with chlo-

rine and hydrogen. Hydrobromic acid, HBr, results. This acid cannot be made in pure condition by the reaction employed in the manufacture of hydrochloric acid, that is, by the decomposition of a bromide by means of strong sulphuric acid, according to the following equation:

$$2KBr + H_2SO_4 = K_2SO_4 + 2HBr$$

The hydrobromic acid as liberated is partially decomposed by the excess of strong sulphuric acid, free bromine and sulphurous oxide being formed. This can be illustrated as follows:

Experiment 77. Take some small crystals of potassium bromide in a test-tube, and pour over them a little strong sulphuric acid. An escape of gas is seen to follow, which has a yellowish color, due to free bromine, the hydrobromic acid itself being a colorless gas.

Pure hydrobromic acid may be made, however, by using phosphoric acid instead of sulphuric acid, and by a reaction illustrated by this equation:

$$PBr_3 + 3H_2O = 3HBr + H_3PO_3$$

Phosphorous bromide is decomposed by water, yielding hydrobromic acid and phosphorous acid. Instead of using pure phosphorous bromide it is customary to add bromine very slowly to a mixture of red phosphorus and water in a suitable apparatus arranged in such a manner that the gas as it escapes may be absorbed in water.

Properties. In most of its important properties hydrobromic acid resembles hydrochloric acid. It is a gas, and very soluble in water. One cubic centimeter weighs .00362 Gm. at 0° and normal pressure. It is readily decomposed by chlorine and it unites with alkalies forming bromides.

Hydrobromic acid and all the soluble bromides give a precipitate when treated with a solution of silver nitrate as shown below:

Experiment 78. Prepare a dilute solution of potassium bromide by dissolving a small crystal in water. Add to this solution

a few cubic centimeters of a dilute solution of silver nitrate. A yellowish white, curdy precipitate forms which soon settles to the bottom of the vessel in which it was produced. This precipitate is not soluble in nitric acid, and to a limited extent only, in dilute ammonia.

The compounds of bromine with hydrogen and oxygen are not of sufficient importance to be taken up in this place in detail. No oxides are known, but two oxygen acids, hypobromous acid, HBrO, and bromic acid, $HBrO_3$, are known. Some of the hypobromites, the salts formed from HBrO, are used as reagents.

IODINE.

Iodine is a very important element resembling chlorine and bromine in certain chemical properties, but is a steel gray solid at the ordinary temperature. It is far less abundant than either chlorine or bromine in nature, occurring in some springs, but mainly in sea water, from which it is taken up by certain seaweeds. The iodine of commerce is largely obtained from the ash produced by burning these weeds. It occurs also in small amount in compounds called iodates, which occur with Chili saltpeter.

History. Iodine was discovered by Courtois, a French chemist, in 1812. It was found in the mother liquors left after the extraction of sodium salts from kelp or the ash of seaweeds. Until recently this kelp, or varec, was the source from which practically all iodine was obtained. A larger proportion is now produced from the mother liquors occurring in the refining of Chili saltpeter. As produced from seaweed iodine is obtained mainly from the coasts of Scotland and northern France.

Preparation. As found in the ash from seaweed, the iodine occurs in the form of an iodide and can be separated just as bromine is from bromides. The following experiments will illustrate this:

Experiment 79. Dissolve a small crystal of potassium iodide in about five Cc. of water in a test-tube. Then add chlorine water, a drop at a time, which produces a brown color, and finally, if

the solution is not too weak, a precipitate of free iodine. An excess of chlorine water discharges the color as in the corresponding case with a bromide, and for the same general reasons.

The decomposition is illustrated by this equation:

$$KI + Cl = KCl + I$$

35.5 parts of chlorine replace 127.0 parts of iodine.

Iodine is liberated, also, by the reaction with manganese dioxide and sulphuric acid, which can be easily illustrated by a simple experiment as follows:

Experiment 80. Mix about a gram of powdered potassium iodide with two or three times this weight of powdered manganese dioxide in a flask of 300 to 400 Cc. capacity. Pour in 5 Cc. of dilute sulphuric acid and heat the flask on a sand-bath. Decomposition of the iodide takes place and deep violet colored vapors fill the flask. The vapors condense in part on the upper and cooler portions of the flask.

The decomposition is illustrated by the equation.

$$2KI + MnO_2 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + I_2$$

On the large scale the reaction is so carried out that the iodine distills over from the decomposing retorts of earthenware or firebrick, and condenses in cold receivers.

Properties. Commercial iodine occurs as a steel gray crystalline solid. In its power of combination with metals iodine is less active than chlorine or bromine. The important properties of the substance may be shown by simple experiments.

Experiment 81. Heat a small crystal of iodine in a test-tube. The iodine vaporizes quickly, so that the whole tube may be filled with the violet colored vapors. That these vapors are heavier than air may be shown by holding the tube in front of a sheet of white paper as a background, and then turning the tube so that the vapor may flow down and show against the paper. When the tube cools, add a little distilled water and shake thoroughly. Iodine is slightly soluble in water, which is shown by the yellow color imparted in this test. To the aqueous solution add a few drops of cold starch paste. A beautiful blue results, due to the combination of the starch with iodine.

Experiment 82. Iodine is much more soluble in alcohol than in water. Powder a small crystal of iodine and transfer to a test-tube. Then add about 2 Cc. of alcohol and shake thoroughly. The iodine dissolves, producing a brown solution known as the *tincture of iodine*. A drop of this tincture added to a beaker of water containing a little starch paste produces a blue color.

Experiment 83. Iodine dissolves very readily in an aqueous solution of potassium iodide, which can readily be shown by adding a small amount of powdered iodine to potassium iodide solution. A dark brown liquid results. This is known as Lugol's solution, or the "compound solution of iodine" of the pharmacopœia, when made with certain definite quantities of iodine, potassium iodide and water. Show that the addition of a great excess of water produces a precipitate in this solution, and that it gives the blue color with starch.

Experiment 84. Dissolve minute crystals of iodine in carbon disulphide, ether and chloroform, and observe the colors of the solutions. Add chlorine water to a very dilute aqueous solution of potassium iodide in a test-tube, until a brown color is formed, and then add several large drops of carbon disulphide and shake. The iodine is taken from the water by the disulphide, imparting to the latter a characteristic color.

Physical Properties. Pure iodine has a specific gravity of 4.95. It melts at about 115° and boils below 200°.

Uses. Iodine is employed in the preparation of iodoform and several iodides used in medicine. It enters into the composition of many organic compounds.

IODINE AND HYDROGEN.

Hydriodic acid, HI, is a well known and important substance, best made by the action of phosphorus and water on iodine by a process analogous to that employed in making hydrobromic acid. When potassium iodide is distilled with sulphuric acid, pure hydriodic acid is not obtained, as a decomposition of this by the excess of sulphuric acid follows, with liberation of iodine.

In its chemical behavior this acid closely resembles hydrochloric and hydrobromic acids, but it is less stable. It decomposes, liberating iodine, according to the equation:

$$2HI = H_2 + I_2$$

At a relatively high temperature, on the other hand, iodine and hydrogen unite to form the acid:

$$H_2 + I_2 = 2HI$$

This is a peculiar reaction which works in both directions and something more will be said about it later. In water the hydriodic acid is extremely soluble, yielding a heavy solution.

Two oxygen acids of iodine are known; one of these is called iodic acid and is represented by the formula HIO_3. It is a white crystalline solid, soluble in water, and is best made by the oxidation of iodine by strong nitric acid. When strongly heated it decomposes, yielding solid iodine pentoxide, I_2O_5, and this in turn dissolves in water reproducing the acid.

$$H_2O + I_2O_5 = 2HIO_3$$

Several iodates are known; sodium iodate is found in Chili saltpeter.

Finally, a more highly oxidized compound of iodine is known and this is called periodic acid, HIO_4. It is a colorless crystalline solid, very soluble in water. Several unimportant compounds with chlorine and bromine are known, and also a singular compound with nitrogen which will be described later.

FLUORINE.

This is a gaseous element of which but little is known in the free state.

Occurrence. It is found in nature in two important mineral compounds. One of these is calcium fluoride, CaF_2, and is called fluorspar. The other is a so-called double fluoride, containing sodium and aluminum, $AlF_3 + 3NaF$, called cryolite. Fluorine is found in bones and especially in the teeth in small amounts.

History. Some combinations of fluorine have been known for many years, but all attempts to isolate the ele-

ment failed until quite recently. Moissan succeeded a few years ago in liberating it by the electrolysis of hydrofluoric acid in a platinum tube at a very low temperature.

Properties. Fluorine is characterized by its remarkably strong affinities. It combines with nearly all elements except oxygen. It attacks glass to combine with its silicon and corrodes metals at the ordinary temperature quickly. Because of these peculiarities chemists have found difficulty in studying it, rather than in decomposing its compounds. At the low temperature of Moissan's experiments it may, however, be set free in platinum. It is a yellow gas which decomposes water instantly, forming hydrofluoric acid and oxygen. Many substances burn with the gas as they would with oxygen. It has recently been liquefied.

FLUORINE AND HYDROGEN.

An important combination of these elements is known. This compound is known as hydrofluoric acid, HF, and is very soluble in water. The solution is now an article of commerce and is sold for several purposes. It is usually prepared by the action of sulphuric acid on calcium fluoride, a native mineral substance found in quantity in several localities. This reaction is analogous to that by which hydrochloric acid is made from sodium chloride by means of sulphuric acid, and may be illustrated by this equation:

$$\underset{\text{Calcium fluoride}}{CaF_2} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Calcium sulphate}}{CaSO_4} + \underset{\text{Hydrofluoric acid}}{2HF}$$

The fact that hydrofluoric acid attacks glass may be shown easily by experiment.

Experiment 85. In a lead dish, having a diameter of 5 centimeters or more, make a pasty mixture of strong sulphuric acid and powdered calcium fluoride. Place the dish on a sand-bath and by means of splinters of wood support over it a square of glass, both surfaces of which have been covered with wax. In the center of one of the waxed surfaces scratch some letters or figures and expose this surface to the action of the fumes which

arise from the dish when it is heated. The temperature must not be allowed to get high enough to melt the wax. After fifteen or twenty minutes remove the glass and scrape off the layers of wax. It will be observed that at the exposed points the figures or letters have become fixed in the glass by its corrosion. Much of our graduated chemical ware is marked in this manner.

Etching is frequently carried out by immersing the glass article, properly protected by wax, in an aqueous solution of hydrofluoric acid or in a mixture of dilute sulphuric acid and powdered fluorspar. No heat is applied, but a longer time must be given to complete the work. This reaction is due to the affinity of the fluorine for an element of the glass, the silicon. Some of this element is dissolved out by the hydrofluoric acid, forming silicon fluoride, SiF_4.

The aqueous solution of the acid cannot be kept in glass or iron vessels. It is handled on the small scale in bottles of hard paraffin or gutta-percha, and in large quantities in barrels coated with paraffin.

Some of the fluorides are becoming important articles of commerce. The native calcium fluoride is largely used as a flux in the smelting of iron ores.

GENERALITIES.

The four elements, fluorine, chlorine, bromine and iodine, constitute a natural group, in which a variation in properties is closely related to a variation in atomic weight. Fluorine, the lightest element, has the strongest affinity for hydrogen and all the metals, but it forms no combination with oxygen. Iodine, the heaviest of the group, forms a stable compound with oxygen, while its combinations with hydrogen and the metals are very easily decomposed. Fluorine decomposes water immediately, iodine not at all. The decomposition by chlorine is much slower than by fluorine, while by bromine it is extremely slow. Of the three well known elements in the group, bromine stands between the lighter chlorine and heavier iodine in all important properties.

In the following table some of the most important rela-

tions of the four elements just considered are pointed out in form suitable for easy comparison. These four elements are spoken of as the halogen group.

	F.	Cl.	Br.	I.
Atomic weight.....	19.00	35.45	79.96	126.97
Molecular weight	38.00	70.90	159.92	253.94
Liquid density.....		1.33	3.18	4.95
Action on water.....	decomposes it very readily	decomposes it in light	decomposes it very slowly	does not decompose
Hydrogen compounds	HF	HCl	HBr	HI
Oxygen compounds...	none known	Cl_2O Cl_2O_3 ClO_2	none known	I_2O_5
Oxygen acids.....		HOCl HOClO $HOClO_2$ $HOClO_3$	HOBr $HOBrO_2$ $HOBrO_3$	$HOIO_2$ $HOIO_3$

NATURE OF ACIDS.

In the foregoing pages the term acid has been frequently employed, and from the experiments made or suggested the general composition and properties of these bodies have been indicated. Hydrochloric acid contains chlorine and hydrogen, hydrobromic acid, bromine and hydrogen, hydriodic acid, iodine and hydrogen, hydrofluoric acid, fluorine and hydrogen. That sulphuric acid also contains hydrogen is evident from many experiments. It will be shown in the next chapter that the very common and important nitric acid is also a hydrogen compound. In general, it may be said here, acids are bodies characterized by containing hydrogen, which may be readily replaced by metals to form a group of compounds known as *salts*. When zinc is dissolved in hydrochloric acid hydrogen escapes and a salt called zinc chloride is produced. When zinc is dissolved in the other acids, zinc bromide, zinc iodide, zinc sulphate, etc., are formed, hydrogen in all cases being set free.

Acids neutralize solutions of bodies known as alkalies and bases, forming, as before, salts. We had an illustra-

tion of this in the experiment in which hydrochloric acid was mixed with the solution of caustic soda. On evaporation, common salt, or sodium chloride, was left. In a similar manner a mixture of hydrobromic acid with caustic soda would yield sodium bromide.

Acids, bases and salts comprise by far the larger number of substances considered in inorganic chemistry. In a following chapter the relations of these bodies to each other and to certain allied substances will be pointed out.

CHAPTER V.

NITROGEN AND THE ATMOSPHERE.

GAS PROBLEMS.

Nitrogen is a gaseous element found in the uncombined state in the atmosphere, and in combination widely distributed through plant, animal and mineral substances. In vegetable tissues it is found in all alkaloids and in all the so-called protein compounds. It occurs in the proteins of the animal kingdom also and in many substances produced by animals. In the mineral kingdom it is found mainly in the substances called nitrates, of which common saltpeter and Chili saltpeter are the best illustrations.

History. Rutherford, in 1772, was apparently the first to suggest by actual experiment the presence in the atmosphere of a gas incapable of supporting life and combustion. Scheele later, about 1774, came to the conclusion that the atmosphere must consist of two distinct gases, but it remained for Lavoisier, in 1775, to make a clear statement of the nature of the two important gases in the atmosphere. The one not supporting life or combustion he called *azote*, while the name *nitrogen* was suggested later by Chaptal.

Preparation. We can obtain nitrogen from the air by separating in some manner the other important element, oxygen, from it. As oxygen enters readily into combination with many substances, while nitrogen is inert, this can easily be done. In illustration, the following experiment may be made:

Experiment 86. We may take advantage of the reaction between phosphorus and oxygen to free the nitrogen from the latter element. To this end dry a very small piece of phosphorus, not larger than a pea, and enclose it in a little cylinder of wire gauze. Attach a piece of iron wire to this cylinder, as a handle, and bend

it into a U shape with one limb longer than the other. The gauze cylinder is attached to the shorter limb. Now ignite the phosphorus, hold it over a vessel of water, and then depress a wide mouth bottle of about 300 to 400 Cc. capacity, over the burning substance, so that the mouth of the bottle dips beneath the surface of the water. A volume of air is thus confined and exposed to the action of the burning phosphorus. In a few seconds the combustion is complete, when it will be found that the level of the water in the bottle is above that in the vessel, this being the case because water must ascend to take the place of the oxygen, united with the phosphorus. After the disappearance of the fumes of phosphoric oxide, by solution, the remaining gas may be tested. Withdraw the wire gauze, leaving the mouth of the bottle still under water, then close the mouth by a glass plate and bring it into the upright position on the table. Test the gas in the bottle as oxygen was tested, using, however, a burning taper or splinter in place of one merely glowing. The flame will be extinguished, showing the inert nature of the gas.

At the beginning of the above experiment the heat of the combustion expanded the air in the bottle and drove part of it out before it was completely acted on by the phosphorus. It follows, therefore, that the gas volume left does not accurately represent the proportion of nitrogen in the original air. It will be shown later that the nitrogen should amount to very nearly four fifths of the whole.

The nitrogen as obtained by the above process is never quite pure, but by more elaborate methods it may be secured from the air in practically pure condition. We may produce it in a pure state by the decomposition of certain compounds containing it, and one such method will be illustrated here, in which we use ammonium chloride:

Experiment 87. Make a mixture of powdered potassium dichromate and powdered ammonium chloride, using four parts by weight of the former to one part of the latter. With this mixture half fill an iron gas pipe retort, about 20 Cm. long and 1.5 Cm. in internal diameter, the arrangement of which is shown in the next figure.

The pipe is closed with a cork and delivery tube, which dips beneath the surface of water in a trough. On applying heat to the retort its contents decomposes with liberation of nitrogen gas, which passes through the delivery tube, and may be collected by displacement of water in the usual manner. Fill several bottles with the gas and test as follows: Remove the bottles with glass plates as in other cases. Into one bottle thrust a burning taper

or piece of wood. Dip into a second a deflagrating spoon containing a small piece of burning phosphorus, and into a third dip

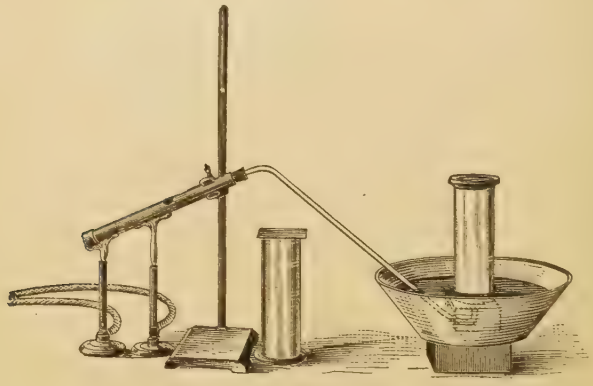


FIG. 14.

a spoon with burning sulphur. The flames will be extinguished in all cases, showing the very inert nature of the gas. On withdrawing the spoon with the phosphorus it may reignite in the air.

The reaction by which the nitrogen was secured in this case is somewhat complex, but by observation of certain details it may be understood. In the progress of the decomposition it will be noticed that vapor of water is given off along with the nitrogen gas, as it condenses in the delivery tube. At the end of the experiment, after cooling the tube, its contents may be shaken out and examined. In place of the red substance taken we have now a green powder, which is found to be partly insoluble in water. By mixing with water in a beaker, stirring a few minutes and filtering, something passes through the filter, leaving the green substance undissolved. By evaporating the filtered liquid we find a residue of potassium chloride, while the green substance the chemist recognizes easily as chromium oxide. We have, therefore, produced in the experiment, nitrogen gas, water, potassium chloride and chromium oxide. Careful investigation shows that

these substances are formed in the proportions illustrated by the following equation:

$$\underset{\text{Potassium dichromate}}{K_2Cr_2O_7} + \underset{\text{Ammonium chloride}}{2NH_4Cl} = \underset{\text{Nitrogen}}{N_2} + \underset{\text{Potassium chloride}}{2KCl} + \underset{\text{Water}}{4H_2O} + \underset{\text{Chromium oxide}}{Cr_2O_3}$$

The combining weight of the potassium dichromate is 294.4, while that of the double part of ammonium chloride taken is 107. We obtain 28 parts of nitrogen, or less than one tenth the weight of the dichromate used. The process therefore is somewhat expensive.

Many compounds containing nitrogen may be decomposed, to liberate this substance, under proper conditions. In case of the compound taken, the ammonium chloride, it is necessary to add something to hold or fix the elements with which the nitrogen is here combined, and the dichromate of potassium answers this purpose by furnishing potassium and oxygen to unite with these elements.

Nitrogen has certain uses in the arts at the present time, but large quantities of the gas in the pure state are not required by them.

General Properties. Nitrogen gas may be condensed to a liquid by application of cold and pressure. The gas is but slightly soluble in water, and is characterized by its extreme inertness or lack of positive properties. It is neither combustible nor a supporter of combustion, but it does unite directly with hot magnesium. A liter of the pure gas weighs 1.251 Gm. under standard conditions.

THE ATMOSPHERE.

The atmosphere is a mixture of oxygen and nitrogen, essentially, with smaller quantities of moisture, argon and carbon dioxide, and traces of other gases. The relation between oxygen and nitrogen has been suggested above, and can be shown by exact experiments. The amount of oxygen may be readily determined by the following,

which is merely a modification of our first experiment on the separation of nitrogen.

Experiment 88. Procure a glass tube, sealed at one end, having a length of about 75 Cm. and an internal diameter of 1.5 to 2 Cm. If it is graduated it will be so much the better for our purpose, but if it is not an approximate graduation may be made as follows: Pour a small measured volume of water into the tube, when held in a vertical position and mark its level by means of a close fitting rubber ring shoved down the tube. Then add the same volume of water and mark the new level as before, and repeat the operation until the whole tube has been divided into equal small volumes. The rings should not be displaced by ordinary handling. Now pour about 20 Cc. of water into the tube and invert it in a deep jar of water. By means of a clamp on a lamp stand, fasten the tube in such a position that the levels of the water inside and outside are the same after the tube has stood long enough to have the air temperature. The tube should have a perfectly vertical position. Note the volume of the air enclosed with reference to the rubber rings. Next scrape off a piece of phosphorus, weighing two or three grams, and fasten it to a thin iron wire, a meter and a half in length, bent in the middle so that the two halves are close together. Now depress the wire with the phosphorus in the jar so that the limb with the phosphorus is brought beneath the opening of the tube. Then pull up the free end of the wire and guide the phosphorus with the fingers of the other hand so that it enters the tube. By means of the outside wire it can now be pulled up to the top of the tube, nearly, and there it should be left about 24 hours. In these manipulations, care must be taken not to bring the end of the tube above the surface of the water in the jar, and so change the air volume once read off. Great care must be taken to prevent the ignition of the phosphorus while handling it. This can be avoided by keeping it wet. When once up in the tube there is no further danger. The phosphorus undergoes slow oxidation and gradually combines with the oxygen present. By the end of 24 hours the reaction will be complete. Then shove down the wire and remove the phosphorus carefully and put it back under water. Observe that the water level in the tube is higher than before. By means of the clamp, and without touching the tube with the hands, depress it until the two water levels are the same again. Read off the gas volume now enclosed. The decrease in volume represents the oxygen only.

Instead of inserting the phosphorus by the method described, the student may find it more convenient to close the end of the long tube, after noting the gas volume, by means of his finger, and then carefully lift it out of the water in the jar and dip it beneath the surface of water in a large bowl. The air volume remains unchanged. The tube can now be inclined to one side

and the phosphorus, scraped and fastened to the wire in the same bowl, can be readily shoved up into the tube. If the wire is soft enough there will be no difficulty in bending it around the end of the tube so that the latter may again be closed by the finger and brought back into the jar and clamped. Before beginning the experiment, a piece of phosphorus of the proper diameter should be selected.

To obtain an accurate result by the above experiment it is essential that the temperature of the gas in the tube at the two readings remain the same, and also that the pressure of the air outside, or the *barometric pressure,* remain unchanged. These conditions are practically never attained and it is therefore necessary to make certain corrections to compensate for these changes. By increase of temperature gas volumes expand, and therefore, if the laboratory is warmer at the time of the second reading than at the first, the volume read off will be high and the loss (or the amount of oxygen) will be made to appear too low. If the temperature at the second reading is lower than before, the residual volume will be low and the oxygen will thus be obtained too high. This effect of temperature can readily be observed by the student by grasping the tube, still clamped in position, in the hand. The heat of the body, thus communicated to it, is sufficient to make a marked depression of the water level in the inside of the tube. Before making readings the tube should, therefore, be handled as little as possible.

Changes in air pressure outside change the inner volume also. An increase in the air pressure, indicated by elevation of the barometer, is communicated through the water and decreases the gas volume in the tube. The increased pressure forces the water down in the jar and therefore, because they are in communication, up into the tube. Following a decrease in barometric pressure the gas volume in the tube will expand. As preliminary to an explanation of the calculations of these corrections let the following experiment be made:

Experiment 89. Suspend a thermometer in such a manner that its bulb hangs within a few centimeters of the middle part of a graduated tube containing some air as in the last experiment. When the temperature appears to be constant, and the volume of

the gas therefore stationary, raise or depress the tube by means of the clamp until the water levels inside and outside are accurately the same. Now, read off the volume of the air as shown by the graduation, read the thermometer and the height of the barometer, which should hang in the immediate vicinity of the other apparatus. The temperature within the tube is assumed to be the same as shown outside. With the water levels the same the pressure on the gas within the tube must be the same as that of the air, as measured by the barometer. With these data at command let the student calculate the reduced volume at the assumed normal conditions of 0° C. and an air pressure of 760 Mm., by the method explained below.

REDUCTION OF GAS VOLUMES.

Correction for Temperature. In comparing gas volumes it is necessary to refer them to some standard temperature, which by common consent is 0° C. As intimated above, all gases expand by increase in temperature, and practically at the same rate. By *rate of expansion* or *coefficient of expansion* we understand the fraction of its volume at 0° which it increases for an increase of 1° in temperature. This rate is the same for an increase from 0° to 1° as it is for an increase from 10° to 11° or from 19° to 20° practically. In other words, it is constant, or so nearly constant that we assume it for our purpose.

Let us represent the volume of a gas measured at 0° by V_0 and the volume of the same gas expanded to the temperature t°, by V_t. What is the relation of V_t to V_0? It is evident that this equation must be true,

$$V_t = V_0 + \text{increase}$$

The increase in volume is made up of three factors, or is the product of three factors. One of these is the rate of expansion defined above, which we will call *r*. The second factor is the number of degrees of temperature through which the expansion takes place, and this we call *t*, while the third factor is the amount of V_0 itself, or in other words is the number of units of volume in V_0. The actual increase in volume for two liters would evidently

be twice as great as for one liter. Our equation therefore becomes,

$$V_{(t)} = V_{(o)} + V_{(o)} \times r \times t,$$

or, by a slight alteration

$$V_{(t)} = V_{(o)} (1 + rt)$$

Now, as intimated, the rate of expansion of all gases is nearly the same and amounts to $\frac{1}{273}$ of their volume at 0°, for each degree of increase. Therefore, $r = \frac{1}{273}$, or, expressed decimally 0.00366. Making this substitution we have,

$$V_{(t)} = V_{(o)} (1 + 0.00366t)$$

This is a fundamental equation and by transformation we get the next one,

$$V_{(0)} = \frac{V_{(t)}}{1 + 0.00366t}$$

Law of Charles or Gay-Lussac. These equations express the principle known as the law of Charles, who first discovered it, or of Gay-Lussac, who determined the rate of expansion of gases with the temperature. According to these observations gases expand, apparently, at a uniform rate from a point 273° below the centigrade zero. This point, —273°, is therefore spoken of as the *absolute zero.*

In illustration of the above equations assume that we have 100 Cc. of air at 0° and wish to know its volume when warmed up to 25°. That is, we wish to find $V_{(t)}$ or V_{25}.

$$\begin{aligned} V_{(25)} &= 100 (1 + 0.00366 \times 25) \\ &= 100 (1 + 0.0915) \\ &= 109.15 \end{aligned}$$

The new volume is therefore 109.15 Cc. Conversely, if we have given this volume at 25° and wish to know

what it becomes when cooled to 0° we use the formula,

$$V_{(0)} = \frac{109.15}{1.0915} = 100 \text{ Cc}$$

As gases contract below zero at the same rate at which they expand above zero these formulas can be used for minus temperatures by change of sign.

Correction for Pressure. Boyle's Law. We learn by experiment that the volume of a gas varies as the pressure changes, but inversely. That is, if the pressure becomes doubled the gas volume is contracted to one half. If the pressure decreases to one half the gas expands to fill double the volume. The relation, that the volume of a gas varies inversely as the pressure on it, was first pointed out by Boyle. The law is sometimes, but wrongly, spoken of as Mariotte's law. If V represents the volume of a certain gas at the pressure P and V′ the volume of the same gas at the pressure P′, it would follow from the above that

$$VP = V'P' = V''P'', \text{ etc.}$$

That is, the product of the volume and the corresponding pressure is a constant. Under certain conditions this law is only approximately correct, but the variations are so slight that for the present purpose they may be neglected. We assume a standard pressure as we do a standard temperature in the measurement of gas volumes and this is usually taken as the average pressure of the air at the sea level, a pressure equivalent to that of a column of mercury 760 Mm. in height. If we let P = 760 Mm. and V the normal volume then it would follow that

$$V = \frac{V'P'}{760}$$

That is, the reduced or normal volume is equal to the

product of the observed volume and the observed pressure divided by 760 Mm., the standard pressure. In illustration, if we read off a volume of 150 Cc. at 740 Mm. pressure, as shown by the barometer or other pressure gauge, the reduced volume must be

$$V = \frac{150 \times 740}{760} = 146.05 \text{ Cc.}$$

From what was said above it is further evident that the pressure of a given volume of gas must vary as the absolute temperature, T. We may write, therefore, with a constant atmospheric pressure, and $t = T - 273°$,

$$V'P' = V_0P_0(1 + \tfrac{1}{273}t) = \frac{V_0P_0}{273}T = RT,$$

when R is the so-called gas constant, and is the same for all gases.

The effect of changes of temperature and pressure are independent of each other; we can make, therefore, either correction first, and on this result calculate the other correction. Both corrections can be introduced in one formula. Let v represent the observed volume, h the observed barometric height and V the volume at 0° and 760 Mm. Then

$$V = \frac{v \quad h}{(1 + 0.00366\ t)\ 760}$$

This formula is used where the gas is measured under a pressure exactly equivalent to that of the barometric height, h. In practice certain modifications may be necessary. The calculation of the results of the last experiment is a case in point. The volume of the gas is read off over water; it is therefore saturated with moisture, which also exerts some pressure, even at low temperature. The air pressure, h, is therefore balanced by the true gas pressure, which we can call p, plus the pressure of the aqueous vapor which we can call w.

$$h = p + w, \text{ therefore } p = h - w.$$

Our formula above then becomes

$$V = \frac{v\ (h - w)}{(1 + 0.00366\ t)\ 760}$$

The tension of water vapor is always expressed in millimeters of mercury, and can be found from a table in an earlier chapter. For three common temperatures it may be given here.

t	w
15	12.7 Mm.
20	17.4 Mm.
25	23.5 Mm.

Suppose now, that in the last experiment we read off a volume of 95.5 Cc. of air saturated with moisture, at a temperature of 20° C., while the barometer stood at 745 Mm. The reduced dry volume would then be found by substitution as follows:

$$V = \frac{95.5\ (745 - 17.4)}{(1 + 0.00366 \times 20)\ 760} = \frac{69486}{815.6}$$

In practice it may not be always convenient or desirable to depress the measuring tube until the levels inside and outside are the same. This is generally the case when gases are measured and operated upon over mercury. A column of liquid stands up in the tube and the pressure of this, also, must be brought into the calculation. The pressure of this column, like that of the aqueous vapor, must be subtracted from the height of the barometer as read off. If this column is mercury, measure its height in millimeters above the level of the mercury in the reservoir below and call it m. The general formula of reduction then becomes

$$V = \frac{v\ (h - m - w)}{(1 + 0.00366\ t)\ 760}$$

In measuring gases over mercury it is generally best to add a minute drop of water to insure that they are *fully* saturated with moisture.

Experiment 90. As an exercise in these calculations let the student measure a gas volume over mercury in an accurately graduated tube, and make all reductions necessary by the last formula. A good barometer and a thermometer should be mounted near the gas tube. The exercise should be repeated until the principle involved is perfectly understood.

Other Air Tests. The amount of oxygen in the atmosphere can be easily and quickly found, by absorbing it from a measured air volume, by means of an alkaline solution of pyrogallol. When great accuracy is desired rather elaborate apparatus must be used, but the method may be illustrated by a very simple experiment.

Experiment 91. Select a long, narrow test-tube, which may be closed by the thumb, and by means of rubber rings, or otherwise, divide it into six equal divisions. Then, holding the tube vertically, pour in enough 10 per cent solution of potassium hydroxide to fill one division. Next incline the tube, and by means of a knife blade introduce about half a gram of dry pyrogallol in such a manner that it will rest on the side of the tube, but above the alkali. Then close the tube firmly by the thumb, and shake it thoroughly. After a minute, invert the tube, with the mouth under water, and remove the thumb. It will be seen that water enters to take the place of the oxygen absorbed by the pyrogallol and alkali. If the tube is allowed to cool to its original temperature, four divisions should remain filled with gas.

The most accurate determination of the amount of oxygen in the atmosphere is made by aid of the eudiometer as described in the chapter on water. A volume of air is measured in the eudiometer over mercury, the proper corrections being made. Hydrogen is then introduced, more than enough to combine with the oxygen present, and the new volume is measured. A spark is next passed through the gaseous mixture as described, and this causes the oxygen to unite with the requisite amount of hydrogen to form water. A contraction follows and after a time the new volume is read off and reduced to normal temperature and pressure. As two volumes of hydrogen unite with one of oxygen, one third of the loss noted is the amount of the latter originally present in the reduced air volume. In 100 volumes of dry air there are 21 volumes of oxygen.

OTHER CONSTITUENTS OF THE ATMOSPHERE.

The amount of nitrogen in dry air was assumed, until quite recently, to amount to 79 volumes in 100, the traces of other gases being very minute. But in 1895 it was found by Rayleigh and Ramsay that a gaseous element resembling nitrogen is also present, and this element has always been included in what has been measured as nitrogen.

Argon.

This is the name which was given to the new element, the amount of which in the air appears to be about 1 per cent. It is especially characterized by great inertness in power of combination, and this accounts for the fact that it had so long escaped recognition. It can not be combined with other elements, by the aid of heat, electricity or other agencies. At a low temperature it has been condensed to a liquid which boils about —186°. At a slightly lower temperature it solidifies. Argon has been found elsewhere as well as in the atmosphere, and more recently other gaseous elements known as helium, krypton, neon and xenon, have been found which accompany argon. The amount of these in the atmosphere is extremely small, but helium has been found more abundantly in the gases escaping from certain springs, and in certain minerals.

Argon is left as a residue when a large body of air is passed over hot copper for the removal of the oxygen and repeatedly over hot magnesium for the removal of the nitrogen. The nitrogen may also be removed by combining it with oxygen by aid of the electric spark and over alkali to absorb the acid products formed. The excess of oxygen is afterward removed by the copper method or by pyrogallol, as described above.

Carbon Dioxide. The air contains about 3 volumes of this gas in 10,000 under normal conditions. But in the atmosphere of crowded cities and in buildings it may be much increased. In the streets it is sometimes present to the extent of 6 or 7 volumes in 10,000, while in

crowded rooms, poorly ventilated, it sometimes reaches 15 volumes in 10,000, or even higher. The gas is produced by processes of respiration and combustion, and is absorbed from the air by the growth of vegetation. The total amount of this gas present in the air is enormously great, being estimated to exceed 3,000 billions of kilograms.

Moisture. The amount of aqueous vapor present in the air varies within wide limits, being largely dependent on the temperature. A cubic meter of air, if fully saturated at 0°, contains 4.87 Gm. of moisture; at 10°, under the same conditions, it contains 9.36 Gm.; at 15°, 12.75 Gm.; at 20°, 17.16 Gm.; at 25°, 22.84 Gm., and at 30°, 30.1 Gm. The air is seldom fully saturated, but often holds 75 per cent of this amount. Such an atmosphere is unpleasantly moist. If the amount of moisture is below 50 per cent of that required for saturation the air appears dry to the skin. When an atmosphere nearly saturated with moisture is suddenly cooled to a temperature below that for which the water present is sufficient for saturation a part of this water must precipitate in the form of rain. On the other hand, if the air remains warm it may hold a very large amount of moisture without precipitating, and through much of our summer weather in the United States this is often the case. Evaporation from the skin cannot take place if the air is already saturated with moisture, and such an atmosphere we describe as a "close" one.

The amounts of moisture and carbon dioxide in the air are best determined by aspirating a given volume of the air through a series of weighed absorbing tubes. The first of these tubes are charged with substances to take up the water; the following tubes contain something to absorb the carbon dioxide, usually caustic potassa. The increase of weight in the tubes, after passing the measured air volume, gives the amounts of the two substances absorbed.

Ammonia. Traces of ammonia, NH_3, are found in the atmosphere at all times, and usually combined as

ammonium carbonate. The ammonia is mostly derived from the decomposition of nitrogenous organic matter and although very small in relative amount, in the whole volume of air it is sufficiently great to be quite important. As it is carried down by the rain it enters the soil and there serves as a valuable food for growing plants. A large part of the nitrogen taken up by certain crops probably comes from the ammonia, or an oxidation product of ammonia, reaching the rootlets in this manner.

Ozone. Traces of ozone, peroxide of hydrogen, and oxides of nitrogen are also often found in the air. These have been referred to already.

Traces of sulphurous oxide and other gases are usually found in the air of cities and besides these, and of great importance, should be mentioned the small amount of organic dust everywhere present. This dust consists partly of living and partly of dead matter. In the living matter are included numerous minute microörganisms which are active in promoting fermentations and putrefaction. The dead organic matter comes largely from the decay and disintegration of animal and vegetable substances.

CHAPTER VI.

COMPOUNDS OF NITROGEN.

Combinations of nitrogen formed by direct union with the gas are rare, but a large number of substances containing nitrogen can be made indirectly. Some of these are of great value and importance.

NITROGEN AND OXYGEN.

Nitrogen combines with oxygen to form five compounds, which are named as follows:

Nitrogen monoxide		N_2O	gas.
Nitrogen dioxide	NO or	N_2O_2	gas.
Nitrogen trioxide		N_2O_3	volatile liquid.
Nitrogen tetroxide	NO_2 or	N_2O_4	volatile liquid.
Nitrogen pentoxide		N_2O_5	solid.

The production of the first and second of these will be shown by experiment.

Nitrogen Monoxide. This substance is known as laughing gas, or sometimes as nitrous oxide, and is readily made by the decomposition of a common crystalline substance known as ammonium nitrate, as shown below. It is made on the large scale at the present time and is sold compressed in cylinders.

Experiment 92. Dry a small flask holding about 250 Cc., and fit it with a perforated cork and long delivery tube bent so as to lead down from the flask, when mounted on a sand-bath, to a trough of water. Pour into the flask 10 to 15 Gm. of dry ammonium nitrate, insert the cork holding the tube, and support the flask on a sand-bath. Now apply heat, very gently at first, which will soon melt the solid ammonium nitrate. Later, gas bubbles will escape from it, and it will appear to boil. Bring the lower end of the delivery tube beneath the surface of water in the pneumatic trough or basin, and collect several bottles of the

escaping gas in the usual manner. As the bottles fill, remove them by aid of glass plates, and stand them on the table in the upright position. Test the gas by burning in it a splinter of wood, some charcoal, sulphur and phosphorus. For the last two use a deflagrating spoon. These substances will burn almost as well as in oxygen. In performing this experiment observe certain precautions. The delivery tube should be wide, the heat should not be allowed to become higher than necessary to decompose the substance, and before removing the lamp the delivery tube should be withdrawn from the water for reasons already explained.

The decomposition of the ammonium nitrate takes place according to this equation:

$$\underset{\text{Ammonium nitrate}}{NH_4NO_3} = \underset{\text{Nitrous oxide}}{N_2O} + \underset{\text{Water}}{2H_2O}$$
$$80 = 44 + 36$$

100 Gm. of ammonium nitrate yield, therefore, 55 Gm. of the oxide. One liter of the gas, at standard temperature and pressure, weighs 1.98 Gm., from which it follows that 100 Gm. of the nitrate will yield nearly 28 liters of the gas.

Properties. At a low temperature the gas may be readily compressed to a liquid. It is slightly soluble in water, one volume of which dissolves about 1.3 volumes of the gas at 0°. It forms no chemical combination in dissolving. At a moderately high temperature the gas is decomposed into its constituents, and this accounts for the fact that combustions follow so readily in it. If metallic sodium is strongly heated with a measured volume of the gas over mercury, combustion follows, and after the residue of nitrogen cools, it will be found to possess the volume of the original gas, from which it follows that the monoxide contains its own volume of nitrogen gas.

Uses. As laughing gas it has been used for many years by dentists and surgeons for the production of mild anæsthesia. When employed for this purpose it must be carefully washed by bubbling through water after leaving the generator.

Nitrogen Dioxide is a substance formed in many reactions in the laboratory, and usually where nitric acid is decomposed by one of the heavy metals. Hydrochloric and sulphuric acids usually yield hydrogen, in contact with metals, but with nitric acid of about 1.2 sp. gr., nitrogen dioxide is liberated. This can take place only through complete decomposition of a part of the acid as shown in the next experiment.

Experiment 93. Arrange a bottle as for generating hydrogen by action of dilute sulphuric acid on zinc, and charge it with about 20 Gm. of copper turnings and 25 Cc. of water. Pour in now through the funnel-tube 25 to 50 Cc. of strong nitric acid. At first red fumes fill the bottle; when these have been driven out connect with a receiving bottle over water, and collect as directed for hydrogen. This experiment should be tried where there is a good circulation of air, as the gas, or rather the product which it forms with oxygen, is very irritating. Collect several bottles of the gas, then fill the generator with water to check the reaction, throw away the acid thus diluted, wash and save any copper left. Test the gas as follows. Plunge a burning splinter in one bottle, and some burning sulphur in another. It will be seen that it does not support combustion. Remove the cover from a third bottle of the gas and bring the mouth of a clean, dry bottle over it. Holding the bottles together invert them so that their contents will mix. Observe that red fumes are formed as the gas comes in contact with the air.

The chemical reaction in this experiment is somewhat complicated, but has been determined by full investigations. It appears from these investigations, which cannot be given in detail here, that the decomposition of the acid by the metal takes place in several stages. But the final results are probably represented by this equation:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

A few pages in advance, when the properties of nitric acid are considered, some illustrations of the general behavior of this acid with metals will be given.

The gas is often called nitrogen dioxide because of the fact that, for a given weight of nitrogen, it contains twice as much oxygen as the first oxide described. The older view of its structure is represented by the formula N_2O_2. It is now well known that this cannot be the formula.

Properties. The gas is very slightly soluble in water and does not combine with alkali solutions. It may therefore be bubbled through a solution of sodium hydroxide to purify it in the method of preparation given above, which as described, does not yield a perfectly pure product.

The gas combines with oxygen to form the substance NO_2 or N_2O_4, which was illustrated in the above experiment. The gas does not support the combustion of wood or sulphur, but if phosphorus, burning brightly, be plunged into it active combustion follows, because in this case the initial temperature is high enough to separate the oxygen from the nitrogen.

Nitrogen Trioxide is not readily obtained in the pure state, but an illustration may be given of its formation.

Experiment 94. Let the student mix about 10 Cc. of strong nitric acid with a gram of starch in a small flask. This is placed on a sand-bath *in a fume closet* and slowly heated. After a time red vapors appear in the flask and the reaction soon becomes violent. The lamp should then be removed. Dense red vapors escape from the flask. These consist of nitrogen trioxide with some tetroxide.

In this experiment the starch decomposes the nitric acid, taking a part of its oxygen to form several complex bodies. The remainder of the nitrogen appears as trioxide mainly. The trioxide dissolves in cold water, giving rise to a body known as nitrous acid:

$$\underset{\text{Nitrogen trioxide}}{N_2O_3} + \underset{\text{Water}}{H_2O} = 2\underset{\text{Nitrous acid}}{HNO_2}$$

Nitrous Acid in the pure state is not important as it is not stable. But it combines with alkalies, as caustic soda or caustic potassa, forming nitrites, which are very important substances for laboratory and manufacturing uses:

$$NaOH + HNO_2 = NaNO_2 + H_2O$$

Nitrites are often made by the *reduction* of nitrates, that is by the removal of oxygen from the latter salts.

Such a reduction may be effected by fusion with lead, as illustrated by this equation:

$$KNO_3 + Pb = PbO + KNO_2$$

All nitrites are readily soluble in water.

Nitrogen Tetroxide. As explained above, this body is formed by the union of nitrogen dioxide with oxygen. The actual composition of the substance varies with the temperature, consisting mainly of N_2O_4 at the ordinary working temperature of 25°C. At a few degrees below this point it may be condensed to a liquid. Nitrogen tetroxide is decomposed by contact with water, forming nitric acid and nitrogen dioxide. In presence of air nitric acid is finally the sole product.

In pure condition it is best made by the decomposition of lead nitrate by heat. The reaction is illustrated by this equation:

$$Pb(NO_3)_2 = PbO + N_2O_4 + O$$

By passing the gaseous products of the reaction through a U tube immersed in a cooling mixture, the N_2O_4 may be condensed to a yellow liquid and thus separated from the oxygen. This liquid boils at 22°, about.

Nitrogen Pentoxide is a laboratory product of no importance in the pure state. It is sometimes called nitric anhydride, and when dissolved in water forms nitric acid, as here illustrated:

$$\underset{\text{pentoxide}}{\underset{\text{Nitrogen}}{N_2O_5}} + \underset{\text{Water}}{H_2O} = 2\underset{\text{acid}}{\underset{\text{Nitric}}{HNO_3}}$$

It is a white, crystalline product, and is usually made by extracting water from nitric acid by means of phosphoric anhydride, P_2O_5. It is not stable and breaks up into oxygen and nitrogen tetroxide.

NITRIC ACID.

Occurrence. This acid is formed in traces in nature when electricity passes through moist air. In combined condition it is found as calcium, sodium, or potassium nitrate. Nitrates are produced in nature by a number of oxidation processes, which take place in the soil and in water and which are of the highest importance, as will be more fully explained some pages in advance.

History. The acid seems to have been first made by distilling a mixture of saltpeter, alum and blue vitriol, and this as early as the ninth century. Later, in the middle of the seventeenth century, it was made by Glauber by a process similar to that still employed, that is, by distilling saltpeter with sulphuric acid. The actual composition of the acid was a subject of lively discussion until after the days of Lavoisier and Cavendish. The latter finally gave the true explanation of its formation and structure.

Preparation. As mentioned, this substance is produced in small traces by certain natural agencies, but in quantity it is always made by the decomposition of some nitrate. We have seen that common salt, or sodium chloride, is decomposed by sulphuric acid, yielding, as one product, hydrochloric acid. In a similar manner saltpeter, or the nitrate of potassium, is broken up by distilling it with sulphuric acid, yielding as the important product nitric acid. We can best illustrate this by the following experiment:

Experiment 95. Arrange a glass retort with a flask as a receiver as shown by the next figure. Charge the retort with 25 to 30 Cc. of strong sulphuric acid and about 50 Gm., of powdered potassium nitrate. Mount the retort on a sand-bath and apply heat, gently at first and then with the full gas pressure. The contents of the retort become thin and give off reddish vapors which pass over into the receiver, kept cold by water, and condense to a reddish yellow liquid; collect 10 to 15 Cc. of the acid liquid and apply tests to it as follows: Transfer it to test-tubes and in one dip a pine splinter. After a time note the appearance of the wood on its withdrawal. Add a little starch to the same tube and heat gently (do this in a fume closet). Observe the decomposition already explained. In a second tube add some copper turnings to

the acid. Observe the gas given off, and the color of the solution formed. To the acid in a third tube add some strong solution

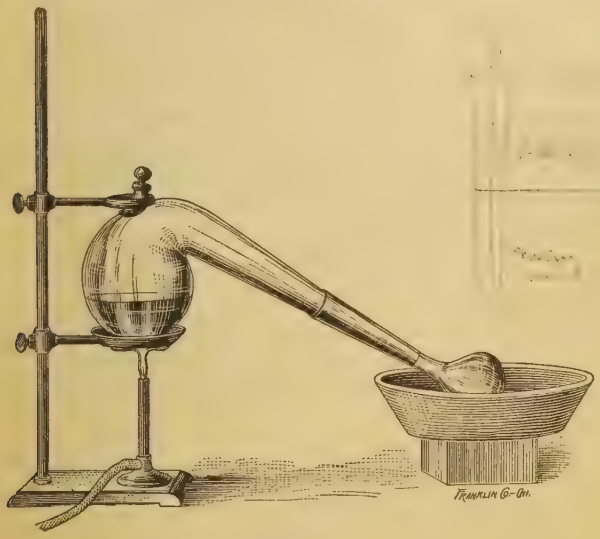


FIG. 15.

of ferrous sulphate, green vitriol, and observe the brown color formed, which disappears rapidly at first, but later remains as a ring in the middle of the liquid column.

The liquid residue in the retort solidifies on cooling and then is removed with some difficulty. It is therefore better to pour it through the tubulure of the retort, while still hot, into a porcelain dish. The retort is then allowed to cool and what remains can be readily washed out.

The substance in the dish should be heated on a sand-bath, in a fume closet, as long as it continues to give off vapors. What is left soon becomes solid on cooling and is easily recognized by the chemist as potassium sulphate. We have therefore here a reaction in which potassium nitrate gives place to potassium sulphate, and free nitric

acid takes the place of the sulphuric. By the use of our symbols we can illustrate this change as follows:

$$\underset{\text{Sulphuric acid}}{H_2SO_4} + 2KNO_3 = K_2SO_4 + \underset{\text{Nitric acid}}{2HNO_3}$$

Nitric acid, it appears, is formed by the decomposition of a nitrate, and conversely, a nitrate can be made by the action of nitric acid on certain other substances, in illustration of which make the following experiment:

Experiment 96. Dissolve about 5 Gm. of potassium carbonate (pearlash) in a little water and add to it some nitric acid, a little at a time. Effervescence begins as the liquids mix. Add the acid slowly as long as gas escapes after thoroughly stirring the solution. Then add a few drops more of the acid and evaporate the liquid resulting in a porcelain dish to complete dryness, stirring well at the end of the operation. Compare the solid substance left, in appearance and taste, with the nitrate used in the last experiment.

From what has been given above it is evident that nitric acid is a very strong and corrosive substance. In the pure form it is not very stable, and therefore it appears in commerce diluted with water. It could not be safely handled under other conditions.

On the large scale the decomposition of the saltpeter is carried out in iron retorts or boilers holding sometimes tons of the raw materials. Sodium nitrate or Chili saltpeter is now commonly used instead of potassium nitrate, as it is much cheaper. The acid fumes which distill over are collected in a series of well glazed earthenware Woulfe bottles, which contain a little water. It is not practicable to make or handle absolute nitric acid. The commercial product always contains some water. Several grades are sold having specific gravities usually from 1.38 to 1.45, corresponding to acids of 61 to 77 per cent strength approximately. A strong red acid is found in the market, known as fuming nitric acid. This acid contains oxides of nitrogen dissolved.

Nitric acid is most characteristically distinguished by its power of oxidation or supporting a kind of combus-

tion. Indeed, there are cases in which it may be made to give up oxygen directly to ordinary combustible substances, as illustrated by the following experiment:

Experiment 97. Place a small beaker on an iron dish containing sand. Pour 20 Cc. of strong fuming nitric acid into the beaker. Grasp a rod of charcoal, about 5 Cm. long and 5 Mm. in thickness, at one end with iron forceps, and ignite the other end in a gas flame. When it is glowing brightly dip the burning end beneath the strong acid in the beaker and observe that the combustion continues with evolution of red fumes in quantity. The oxygen of the acid is in part taken by the charcoal, while the rest is held by the hydrogen and nitrogen. In performing this experiment care must be taken to avoid touching the glass with the hot charcoal. As this might break it and spill the acid, the sand is placed beneath the beaker to catch the acid if this accident should happen. The experiment must be made in a fume closet, as the gases given off are very offensive.

In any experiment with nitric acid in which red fumes are abundantly given off we may be certain that oxidation is taking place. That is, a part of the acid, at least, is undergoing decomposition by which oxygen is given to some other substance. In the above case the charcoal burns at the expense of the oxygen, so furnished, as well as it does by the aid of atmospheric oxygen.

This property of oxidation is not confined to the acid alone, but is found in marked degree in many of the combinations of nitric acid, or nitrates, as can be shown by the following experiment with potassium nitrate:

Experiment 98. Dry and powder about 10 Gm. of potassium nitrate. Pour it into an ordinary dry test-tube, and heat this carefully in the flame of the Bunsen burner. The nitrate soon begins to melt, and finally all of it becomes liquid. Continue to heat it carefully in the flame, moving the tube to and fro, to evenly distribute the heat. Then drop in a small piece of charcoal and observe that it soon ignites and burns with a hissing noise. When the first piece is consumed add a second, which burns in the same manner, the tube being still held in the flame. Then drop in a small fragment of sulphur, which likewise burns at the expense of the oxygen taken from the nitrate. In performing this experiment the tube should be heated over a sand bath to catch the liquid saltpeter in case of breakage, which, however, need not happen if care is taken.

The above experiment illustrates in a very marked

manner the oxygen furnishing power of a nitrate. Niter, either potassium nitrate or sodium nitrate, is used with sulphur and charcoal in the production of ordinary gunpowder, which contains the three substances in certain proportions. Nitric acid is employed in the arts mainly on account of its oxidizing properties, rather than because of its acidity.

A few metals resist the action of strong nitric acid, most of them are dissolved forming nitrates, while a few are converted into oxides without solution. This is true of tin and antimony as will be shown later by experiment.

The behavior of nitric acid in dissolving metals is not perfectly clear, and several theories have been advanced to account for it. To discuss these would be out of place in an elementary book. But one view which has long been advocated may be illustrated by considering the reaction between copper and nitric acid. It is assumed that this takes place in two stages. We have first, apparently, what may be called the *normal* reaction between a metal and an acid, that is, a solution of the metal with liberation of hydrogen, as follows:

$$\underset{\text{Copper}}{Cu} + 2\underset{\text{acid}}{HNO_3} = \underset{\text{nitrate}}{Cu(NO_3)_2} + \underset{\text{Hydrogen}}{H_2}$$

This hydrogen, however, instead of escaping in the free state as it does from sulphuric acid and zinc, seems to react on the excess of nitric acid present so as to decompose it. Hydrogen in this condition is called nascent hydrogen, and because of its powerful attraction for oxygen is capable of acting as a reducing agent. At any rate, it is absorbed by the acid, and decomposition products of the latter escape. The reaction here is probably represented by this equation:

$$\underset{\text{Hydrogen}}{3H_2} + 2\underset{\text{acid}}{HNO_3} = \underset{\text{dioxide}}{2NO} + \underset{\text{Water}}{4H_2O}$$

By combining the two equations we have the one given some pages back:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

According to other views the reaction is possibly expressed by these equations:

$$2HNO_3 + 3Cu = H_2O + 3CuO + 2NO$$
$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O$$

With certain metals and dilute nitric acid this assumed reduction by nascent hydrogen seems to go much further, leaving ammonia as the final product. Dilute nitric acid and zinc seem to react on each other in this way:

$$4Zn + 8HNO_3 = 4Zn(NO_3)_2 + 4H_2$$
$$4H_2 + HNO_3 = NH_3 + 3H_2O$$

By combination we have finally:

$$4Zn + 9HNO_3 = NH_3 + 4Zn(NO_3)_2 + 3H_2O$$

The ammonia remains combined with the excess of acid as ammonium nitrate.

Physical Properties. Absolute nitric acid has the specific gravity of 1.53 at 15°. It mixes with water in all proportions and decomposes on heating. The pure strong acid begins to boil at about 86° but decomposes into water, oxygen and nitrogen tetroxide. Under the normal pressure an acid of 68 per cent strength distills without change. The concentrated acid does not dissolve iron and may therefore be shipped in iron drums.

Uses. Nitric acid is employed in many ways. A great deal is used in making nitro-celluloses and nitro-glycerol for explosives. Much is used also in making nitro-benzene and allied bodies employed in the color industries. Many nitrates are made by the solution of metals, carbonates or oxides. These nitrates are, in some cases, employed as oxidizing agents. With hydrochloric acid, nitric acid yields a valuable solution known as *aqua regia*, referred to below.

Nitrates. The nitrates found in many places in nature are produced usually by a series of oxidation processes

from animal or vegetable matter containing nitrogen. This matter reaches the soil often in the form of animal waste or excreta. The changes which it there undergoes by which its nitrogen becomes combined with oxygen are largely the result of the action of minute microscopic vegetable cells known as bacteria. Many of these bacteria have the power of decomposing nitrogenous organic matter in such a manner that in presence of oxygen the nitrogen becomes united to it. Soils become enriched in this manner, as the nitrates are among the best foods for growing plants. In many cases it is probable that the formation of ammoniacal compounds from more complex organic substances precedes the oxidation stage, or production of nitrites and nitrates. This is usually the case in the decomposition of sewage in streams. Urea and other organic bodies are broken down through bacterial agency and ammonia results. In presence of sufficient air this ammonia later gives place to nitrites and nitrates. If this nitrification in the soil takes place in the presence of calcium bicarbonate, which is a common condition, calcium nitrate results. This salt is very soluble and may be carried through the soil to appear later on the sides of caverns as *cave niter*. The deposit in the Mammoth Cave is an illustration. Certain nitrates often appear as an efflorescence on the surface of soil in hot countries. In India such efflorescence, mainly potassium nitrate, is abundant enough to be collected as an article of commerce. The great beds of sodium nitrate in western South America were possibly produced by the oxidation of decaying marine vegetation, but by what agencies cannot now be fully explained. These deposits furnish a large part of the niter in commerce to-day.

Aqua Regia.

This is a mixture of 2 to 3 volumes of strong hydrochloric acid with 1 volume of nitric acid. A decomposition takes place by which two products, known as nitrosyl chloride, $NOCl$, and nitroxyl chloride, NO_2Cl, are formed. This mixture has strong solvent properties, as

metals and ores may be dissolved in it which cannot be dissolved by either nitric or hydrochloric acid alone. It is therefore a valuable reagent in the laboratory, as will appear later.

NITROGEN AND HYDROGEN.—AMMONIA.

Although several compounds of hydrogen with nitrogen are known, only one of them, ammonia, is technically important. This substance occurs in small amounts in air and water, but usually in combination with something else.

History. Combinations of ammonia were known to the alchemists. One of the most important of these, known as sal ammoniac, was obtained by many different processes, and finally by distillation of animal refuse. The carbonate of ammonium resulted from this distillation, and this on treatment with hydrochloric acid furnished the chloride or sal ammoniac. In 1774 Priestley found that this substance when distilled with lime yields a gas, extremely soluble in water and which may be easily decomposed by the electric spark. The composition of this gas was determined by Davy and others. It is represented by the formula NH_3.

Preparation of Ammonia. Ammonia in the free gaseous condition has been made by the direct combination of its elements through the aid of the electric spark. But this preparation has no practical importance. On the large scale, and in laboratory experiments, it is best made by the decomposition of certain of its compounds, called salts of *ammonium*. This is illustrated by the next experiment.

Experiment 99. Arrange a glass flask and Woulfe bottles as in the production of hydrochloric acid, some pages back. Each Woulfe bottle should contain about 100 Cc. of distilled water. In the flask mix about 30 Gm. of ammonium chloride and the same weight of slaked lime. Add enough water to make a thick liquid mixture on shaking. Close the flask, make the connections and apply a gentle heat, which may be gradually increased. A gas is given off from the heated mixture, which passes over and

collects in the water of the first Woulfe bottle mainly. Some reaches the second bottle, and little or none the small flask.

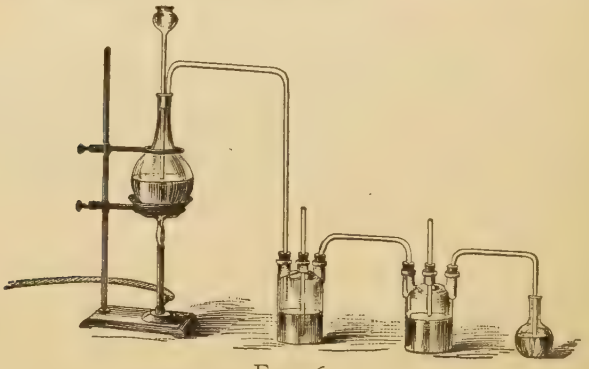


FIG. 16.

After the application of strong heat during half an hour, detach the bottles and test their contents as given below.

Experiment 100. Take half a test-tube full of the liquid from each of the two Woulfe bottles and the small flask, and add to each *2 drops* of an aqueous solution of methyl orange (1:1000). This solution imparts a yellow color with alkalies, which is characteristic. In the liquid from the first Woulfe bottle the reaction should be strong, but much weaker in the others. Add dilute hydrochloric acid now to each test-tube, *a drop at a time,* and observe that in the first case many drops may be necessary to change the color from yellow to pink, but that in the second and third very much less is necessary. Acids impart a pink color to solutions of methyl orange. Next repeat the same experiment, using *10 drops* of a weak alcoholic solution of phenol-phthalein (1:1000) instead of the methyl orange. A deep crimson red color is now obtained with the first test-tube, and weaker shades with the others. When hydrochloric acid is added these colors disappear. Alkalies in general give a red color with phenol-phthalein, but in acids there is no color reaction. These experiments prove the strong alkalinity of the ammonia solution.

Experiment 101. Thoroughly clean three small porcelain evaporating dishes. In one pour about 10 Cc. of the ammonia solution from the first Woulfe bottle. In another take about the same volume of dilute hydrochloric acid, while in the third equal volumes of the ammonia solution and dilute hydrochloric acid are mixed. During the mixing a great volume of white

fumes is produced. Evaporate the three solutions *slowly* on a sand-bath. In the case of the first no residue will be left. The same is true of the second, or hydrochloric acid solution, showing the complete volatility of both of these products. But in the third case, with the mixture, we have left a white residue, which is identical with the ammonium chloride used in the experiment on the production of ammonia. It appears, therefore, that while ammonia and hydrochloric acid are extremely volatile, the product of their union is not, or at any rate, but slightly at the temperature employed. That it is volatile at a higher temperature is shown next, by heating the dish containing the residue more strongly. Dense white fumes are given off, leaving practically nothing in the dish. *All of these experiments must be made in the fume closet.*

The above experiments illustrate the method by which ammonia is obtained on the large scale. Crude ammonium chloride, produced as a by-product in the manufacture of illuminating gas, is distilled with slaked lime, and the gas given off is collected in water. An impure ammonia water is thus made, which is saturated with hydrochloric acid yielding ammonium chloride, not yet pure, but much better than the first crude substance. As this substance is volatile it may be greatly purified by sublimation. The sublimed salt is sent into commerce and used for many purposes. If this sublimed salt is heated again with slaked lime a very nearly pure ammonia gas is given off which may be absorbed in distilled water, yielding a concentrated ammonia solution. By neutralizing this with pure hydrochloric, nitric or sulphuric acid we obtain, on evaporation, pure chloride, nitrate or sulphate of ammonium.

In many large chemical works at the present time pure ammonia water is obtained in one operation from gas liquor. Soft coal contains a little nitrogen, and in the manufacture of illuminating gas by the distillation of such coal the nitrogen becomes converted into ammonia which is carried along with the gas until a large washing tank, called the hydraulic main, is reached. Here the very soluble ammonia dissolves and combines with carbonic acid and hydrogen sulphide from the gas, to form carbonate and sulphide of ammonium. The water in this hydraulic main has to be frequently renewed. To

recover the ammonia from it, it is run into large boilers, mixed with slaked lime and distilled. The lime decomposes the ammonium salts, setting free ammonia gas, which passes through a series of cooling pipes and small washing reservoirs and is then absorbed in distilled water.

The changes referred to above may be represented by equations:

$$\underset{\text{Slaked lime}}{CaO_2H_2} + 2\underset{\text{Ammonium chloride}}{NH_4Cl} = \underset{\text{Calcium chloride}}{CaCl_2} + 2\underset{\text{Ammonia}}{NH_3} + 2\underset{\text{Water}}{H_2O}$$

$$\underset{\text{Ammonia}}{NH_3} + \underset{\text{Hydrochloric acid}}{HCl} = \underset{\text{Ammonium chloride}}{NH_4Cl}$$

$$\underset{\text{Ammonia}}{NH_3} + \underset{\text{Nitric acid}}{HNO_3} = \underset{\text{Ammonium nitrate}}{NH_4NO_3}$$

$$2\underset{\text{Ammonia}}{NH_3} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Ammonium sulphate}}{(NH_4)_2SO_4}$$

Finally, we sometimes speak of the solution of ammonia in water as ammonium hydroxide, NH_4OH, which is $NH_3 + H_2O$. If we may *assume* that this body actually exists in solution, then our reactions should be written after this manner:

$$\underset{\text{Ammonium hydroxide}}{NH_4OH} + \underset{\text{Hydrochloric acid}}{HCl} = \underset{\text{Ammonium chloride}}{NH_4Cl} + \underset{\text{Water}}{H_2O}$$

We have here a behavior analogous to that by which we obtained sodium chloride from hydrochloric acid and sodium hydroxide, or caustic soda. The solution of ammonia gas in water possesses the properties of sodium and potassium hydroxides in a marked degree, as will be shown later. The term *caustic ammonia* has been sometimes applied to the solution.

Other important properties of the gas remain to be shown. For this purpose we may decompose more ammonium chloride with slaked lime, but the gas may be

obtained more conveniently by heating the strong solution, or commercial ammonia water. The following experiment will illustrate this:

Experiment 102. Fit a flask holding about 300 Cc. with a perforated stopper, through which pass a straight glass tube about 20 Cm. in length. Pour about 50 Cc. of the strongest ammonia water of the laboratory into the flask, close it as explained, and then support it on a sand-bath in a stable position, with a small ring of a lamp stand or a clamp around the neck of the flask. Then apply heat. This will cause the ammonia gas to escape from the solution and pass out through the tube. When the escape of gas becomes rapid as shown by the apparent boiling in the flask, hold a *dry* bottle over the open end of the tube, mouth downward, so that the gas may enter and force the air out. As the gas is but little more than half as heavy as air, it may be collected readily in this manner. The tube should reach nearly to the bottom of the inverted bottle. After a few minutes the escape of the gas into the air will show that the bottle is full. Lift it up carefully and close the mouth with a glass plate. It may be then placed, mouth still downward, on a table, while a second bottle of the gas is being collected in the same manner. Remove the second when full, and collect finally a third, giving to this more time than to the others. Remove this bottle, close it quickly with a glass plate, and bring the mouth of the bottle, still held downward, under water in a basin. Then remove the plate, when it will be noticed that the water rushes up and nearly or quite fills the bottle. Had the air been quite expelled in the collection of the gas, the water should completely fill the bottle, showing the quick absorption of the gas by the water. Apply a flame test to one of the other bottles. To this end lift the bottle from the table, mouth still down, and insert a burning taper. It will be extinguished and no flame will remain at the mouth, showing that the gas is neither combustible as is hydrogen, nor a supporter of combustion, as oxygen. With the third bottle of the gas make this experiment: Lift it from the plate and push up into it a strip of perfectly dry red litmus paper. The change of the color to blue will not be rapid. Then moisten a piece of red litmus paper in fresh water which has not been exposed to the ammonia fumes, bring this to the bottle and observe that the change to blue is immediate. The dry gas is not an alkali but becomes so in the presence of moisture.

Properties. At the temperature of 0° C. and under a pressure of 760 Mm. water absorbs about 1,150 times its volume of the gas. A cubic centimeter of water absorbs, therefore, over a liter of the gas. At 30° nearly 500 volumes are absorbed by one volume of water. It

will be seen in what follows that ammonia solution is a reagent of great value in the laboratory, as it is employed for many purposes. The gas is also readily soluble in alcohol and the solution so made has several applications.

At a low temperature dry ammonia gas may be readily condensed to the liquid form and is then usually called anhydrous ammonia. At a temperature of 15° a pressure of about seven atmospheres is required for the condensation. This liquid boils at a temperature of —38°. Like all condensed gases, anhydrous ammonia absorbs a large amount of heat on passing from the liquid to the gaseous condition, and advantage is taken of this fact in refrigerating or in the production of ice. To accomplish this the condensed ammonia is allowed to expand from strong storage tanks into a system of pipes. These pipes may be arranged around the walls and ceilings of rooms to be cooled, or they may be built in more compact form and immersed in a brine reservoir. In this case the brine becomes cooled to a low temperature and if it is pumped into pipes it may be made to circulate through rooms or buildings where cooling is desired. The cold brine reservoir may also be used in the production of artificial ice. It is simply necessary to immerse tanks of distilled water in the brine and allow them to remain there a day or more. The water freezes to a block of clear, pure ice, which is easily removed. The brine for this purpose must have a temperature of —5° to —10° centigrade. The expanded ammonia is compressed again by powerful pumps and so used continuously.

One liter of ammonia gas under standard conditions weighs 0.775 Gm. The specific gravity referred to air is 0.597; it is therefore one of the lightest gases known. It does not support combustion and can be burned only with difficulty. The composition of the gas may be easily determined by decomposing it with the electric spark. This yields one volume of nitrogen to three volumes of hydrogen, which may be shown in a eudiometer similar to the one used in the analysis of water.

Hydroxylamine.

This is a substance which may be looked upon as ammonia, NH_3, in which one atom of hydrogen is replaced by the group OH, called the hydroxyl group. It is an unstable crystalline compound which decomposes very readily. Its solution in water is more stable and the salts, which may be compared with the ammonium salts, are easily made and preserved. The hydrochloride, $NH_2OH.HCl$, is the most important. A reaction by which it is often made depends on the reduction of the gas NO by nascent hydrogen.

$$2NO + 3H_2 = 2NH_2OH$$

Hydrazine.

This is a compound having the formula N_2H_4 and made by decomposition of certain complex organic compounds. It is not stable in the free condition, but occurs as a sulphate, $N_2H_4H_2SO_4$. This sulphate may be decomposed by alkalies yielding a hydrate, $N_2H_4H_2O$, which is a liquid resembling ammonia in some properties. With acids this hydrate yields well defined salts. Some organic derivatives of hydrazine are bodies of great practical importance.

Hydronitric Acid.

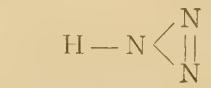
This is a peculiar compound discovered in 1890 and since carefully studied, having the formula HN_3. It is usually made by a series of complex reactions which cannot be explained here, but certain simpler reactions also lead to it. Sodium amide is made first by passing dry ammonia over sodium in a heated porcelain tube:

$$Na + NH_3 = NaNH_2 + H$$

When this reaction is complete a current of dry nitrous oxide is passed through the tube, acting on the amide in this way:

$$NaNH_2 + N_2O = NaN_3 + H_2O$$

The sodium nitride, NaN_3, distilled with dilute sulphuric acid yields free hydronitric acid, or azoimide. In the pure condition the acid is a clear mobile liquid which explodes spontaneously with great violence. It boils at 37°. In water solution it is more stable. It forms salts with most of the metals, on some of which it has a marked solvent action, even attacking gold. It is a poison and destroys the skin rapidly. The odor of the acid is extremely disagreeable. When inhaled the vapor produces violent headache. The salts are called nitrides and in many respects they resemble chlorides. The structure of the acid is probably



NITROGEN AND THE HALOGENS.

Nitrogen forms compounds with chlorine, bromine and iodine, which are all very singular in this respect that they are explosive to a high degree. Of these the iodine compound is most easily made and with safety.

Experiment 103. In a small porcelain dish rub about half a gram of iodine to a fine powder and cover it with a few cubic centimeters of strong ammonia water. Stir repeatedly with a glass rod and after half an hour wash the contents of the dish into two filters. This residue consists of a dark powder, commonly called nitrogen iodide. Wash it on the filters with a little alcohol to remove any unchanged iodine, and then displace the alcohol by washing with water several times. Remove the filters from their funnels and hang them up to dry. It will be found that when the product is perfectly dry the slightest agitation is sufficient to explode it, with a sharp report.

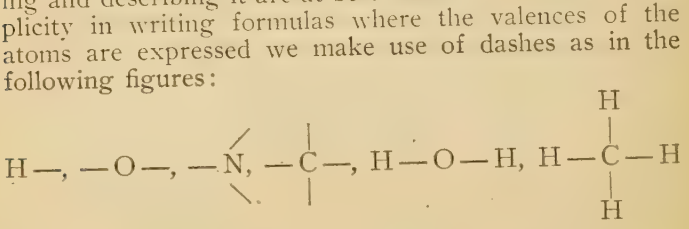
There has been some uncertainty regarding the composition of these explosive bodies, and it appears that under different conditions different products are obtained. What is commonly called nitrogen iodide is probably a mixture of NI_3 and NHI_2. The chlorine compound is a yellowish liquid having the composition NCl_3, probably.

FURTHER THEORETICAL CONSIDERATIONS.

In the third chapter an outline of the atomic theory was presented and it will now be in place to introduce other points of a theoretical nature, as the student has become familiar with the preparation and properties of several new and important substances.

The conception of atoms and molecules has been explained, and it was shown that the combination of atoms in these molecules takes place in definite and fixed proportions. In all cases 23 parts of sodium combine with 35.5 parts of chlorine; 39.1 parts of potassium combine with 35.5 parts of chlorine. Besides these no other combinations of sodium, potassium and chlorine are known. In these cases an atom of one element combines with an atom of the other. An atom of hydrogen weighing 1 combines with an atom of chlorine weighing 35.5 and the result is a molecule of hydrochloric acid with a weight of 36.5 on our arbitrary scale. But when we come to consider the combination of oxygen with hydrogen we find that the amount of the latter which unites with the atomic weight or 16 parts of oxygen, to form water, is just twice as great as the amount which combines with 35.5 parts of chlorine. The oxygen atom appears to have, therefore, double the combining power of the chlorine atom. The amount of hydrogen which combines with one atom of nitrogen to form ammonia is three times that which combines with 35.5 parts or one atom of chlorine, and the amount of hydrogen which combines with one atom of carbon to form a compound known as marsh gas, or methane, is just four times that which will combine with one atom of chlorine. The combining powers or *valences* of the ultimate atoms are therefore different and a study of the whole number of atoms known shows that some resemble hydrogen or chlorine, and these are called *univalent;* some resemble oxygen and are called *bivalent;* some resemble nitrogen and are called *trivalent;* some resemble carbon and are called *quadrivalent*, while other atoms have still higher powers of combination. Of the real nature of this

valence we know nothing and our methods of representing and describing it are at best crude. For sake of simplicity in writing formulas where the valences of the atoms are expressed we make use of dashes as in the following figures:



But there are many cases in which elements combine with each other in more than one proportion, cases in which, apparently, there are multiple combining weights. It will be shown that two oxides of carbon may be prepared. One of these is known as carbon monoxide, and the other as carbon dioxide. By exact analysis it has been shown that the ratio of the carbon to the oxygen in the first of these is 1 : 1.333, while in the second it is 1 : 2.666. That is, we have for a given weight of carbon twice as much oxygen in one case as in the other. Two oxides of nitrogen were prepared, and it was explained that three others are known. An interesting fact was shown by the analyses which chemists made of these. The ratios of nitrogen to oxygen in the five compounds are given in the following table:

	N	O
1st	1	0.5714
2d	1	1.1428
3d	1	1.7142
4th	1	2.2857
5th	1	2.8571

The proportions of oxygen in these compounds stand to each other in the relation, 1, 2, 3, 4 and 5. Two oxides of sulphur are known also, in which the amounts of sulphur present stand to each other in the exact relation of 2 to 3.

In investigating fully these three classes of compounds it soon becomes apparent that the union of oxygen with

nitrogen, carbon or sulphur takes place always as here represented, and such facts give the strongest support to the atomic theory.

But analysis shows and the above table illustrates another point. It appears that nitrogen, under different conditions, has different capacities for holding or combining with oxygen, and we express this by saying that the valence of the nitrogen varies.

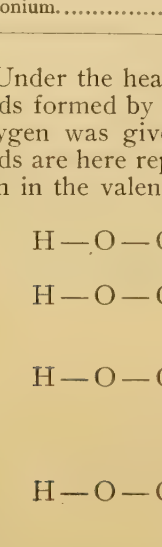
Nitrogen is not the only element in which the valence or capacity for combination is variable. This seems to be, indeed, the rule rather than the exception and an attempt is made in the accompanying table to show the variations in valence in the more important elements:

TABLE OF VALENCE.

Name.	Symbol.	Valence.						
Aluminum	Al			III				
Antimony	Sb			III		V		
Arsenic	As			III		V		
Barium	Ba		II					
Bismuth	Bi			III		V		
Boron	B			III				
Bromine	Br	I		III		V		VII
Cadmium	Cd		II					
Calcium	Ca		II					
Carbon	C		II		IV			
Chlorine	Cl	I		III		V		VII
Chromium	Cr		II	III	IV		VI	
Cobalt	Co		II		IV			
Copper	Cu	I	II					
Fluorine	F	I						
Gold	Au	I		III				
Hydrogen	H	I						
Iodine	I	I		III		V		VII
Iridium	Ir		II		IV			
Iron	Fe		II	III	IV			
Lead	Pb		II		IV			
Lithium	Li	I						
Magnesium	Mg		II					
Manganese	Mn		II		IV			(VII)
Mercury	Hg	I	II					
Molybdenum	Mo		II	III	IV		VI	
Nickel	Ni		II		IV			
Nitrogen	N	I		III		V		

Name.	Symbol.	Valence				
Oxygen	O		II			
Phosphorus	P			III	V	
Platinum	Pt		II		IV	
Potassium	K	I				
Selenium	Se		II		IV	VI
Silicon	Si				IV	
Silver	Ag	I				
Sodium	Na	I				
Strontium	Sr		II			
Sulphur	S		II		IV	VI
Tellurium	Te		II		IV	VI
Thallium	Tl	I		III		
Tin	Sn		II		IV	
Titanium	Ti				IV	
Tungsten	W		II		IV	VI
Uranium	U				IV	VI
Zinc	Zn		II			
Zirconium	Zr				IV	

Under the head of the compounds of chlorine a list of acids formed by the union of chlorine with hydrogen and oxygen was given. The names and formulas of these acids are here repeated and by means of dashes the variation in the valence of the chlorine is indicated.



H—O—Cl — hypochlorous acid.

H—O—Cl=O — chlorous acid.

H—O—Cl(=O)(—O) — chloric acid.

H—O—Cl(=O)(=O)(—O) — perchloric acid.

In the above formulas the hydrogen has always a valence of one and the oxygen a valence of two. The formulas indicate that the oxygen by its double combin-

ing power links the hydrogen to the chlorine. In the first formula the chlorine has a valence of one; in the second of three; in the third of five; in the fourth of seven. Through this increase in valence the chlorine is able to hold more and more oxygen, but, as already suggested, of the nature of this valence and the reasons for its variations we know nothing.

Graphic Formulas. Formulas written like the above with the symbols detached and separated by dashes are called graphic or structural formulas. It is intended to represent by them the manner of combination of the atoms, that is to show which are linked or joined in the molecule. Formulas in which no attempt is made to show structure or the mode of combination are called empirical formulas. For economy of space these are commonly employed, but graphic formulas are exceedingly valuable and in many cases almost indispensable in clearly representing reactions. Their widest application is found in explaining the structure of complex organic compounds, but even in representing comparatively simple substances their use is apparent. Sulphuric acid is commonly represented by the formula H_2SO_4, but experiment shows that the atoms of hydrogen are linked to the sulphur by aid of oxygen. We indicate this view then, by the more complete formula:

$$\begin{matrix} H-O-S=O \\ H-O-S=O \end{matrix}$$

The nucleus atom of sulphur is shown here as having a valence of six. Each oxygen atom has a valence of two and each hydrogen atom a valence of one. Such formulas will be frequently used in what follows but the student must remember that all such attempts to indicate structure are at best insufficient.

Molecules are formed by aggregations of atoms in space of three dimensions, and not in two dimensions as we are for convenience obliged to show them, and in no case, as yet, is our knowledge accurate enough to indi-

cate more satisfactorily the space relations of these atoms than is suggested above for sulphuric acid.

The acids referred to above are qualitatively alike; they all contain hydrogen, chlorine and oxygen. To distinguish between them we employ certain prefixes and terminations, and the student will observe that the same are used in many similar cases. These are:

hypo —— ous.
—— ous.
—— ic.
per —— ic.

It will be remembered that we have nitrous and nitric acids, and later hyposulphurous, sulphurous and sulphuric acids, hypophosphorous, phosphorous and phosphoric acids, and others distinguished in the same manner will be mentioned. The four chlorine acids, the sulphur acids, and the phosphorus acids differ exactly in the same manner, and that is in the valences of the characteristic elements present, and consequently in the amount of oxygen held. The acids having the lowest amount of oxygen are in all cases designated as *hypo—ous* or *—ous* acids, while those with more oxygen or with greater valence are called *—ic* acids. The prefixes *hypo* and *per* (or hyper) are from Greek prepositions meaning respectively *less than, under, below,* and *more than, over, above.* The terminations *ous* and *ic* are arbitrary indications of less or greater valence. A *hypo* acid is therefore one in which the characteristic element (the chlorine, sulphur, phosphorus, etc.) has a lower valence than it has in the *ous* acid. In the *ous* acid the valence is less than in the *ic* acid, and in the *ic* acid it is lower than in the *per—ic* acid.

It has been stated already that a salt is formed by replacing the hydrogen of an acid by a metallic atom. Salts formed from acids containing but two elements, binary acids, take the termination *ide.* Thus, from hydrochloric acid, HCl, we obtain chlorides, NaCl, KCl, $FeCl_2$ and others. From hydrobromic acid we have bromides, from hydriodic acid we have iodides. On the

other hand, if we consider the so-called ternary acids, those with three elements, as were illustrated above, we have, on replacement of the hydrogen, salts corresponding to these acids. The nomenclature of the salts may be briefly indicated as follows:

hypo—ous	acids yield	hypo—ite	salts
ous	acids yield	ite	salts
ic	acids yield	ate	salts
per—ic	acids yield	per—até	salts

Thus, we have potassium chlorate corresponding to chloric acid, and sodium hypochlorite corresponding to hypochlorous acid. These designations are arbitrary but the student should make himself familiar with them as early as possible, as they are of frequent occurrence throughout the book.

CHAPTER VII.

SOME LAWS OF CHEMICAL ACTION. THE BEHAVIOR OF MASS. REACTIONS IN SOLUTION.

CHEMICAL EQUILIBRIA—MASS ACTION.

In the last few chapters chemical changes have been represented by equations which, it was explained, express the results of the reactions in the simplest terms. These equations bear some resemblance to algebraic equations as they are written, but the resemblance is in a measure superficial only. The sign of equality usually employed in our chemical equations has a different significance from that of the same sign in the algebraic equation. In the expression

$$(a + b)^2 = a^2 + 2ab + b^2$$

the members on the two sides are equivalent and the order may be reversed with perfect propriety:

$$a^2 + 2ab + b^2 = (a + b)^2$$

Consider for a moment a simple chemical equation, as:

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

The members on the two sides of the equality sign are equivalent to each other in a limited sense only. A better sign, and one now frequently used, is the $\rightarrow$, which means *leads to* or *forms*. Zinc and sulphuric acid when mixed lead to zinc sulphate and hydrogen, but as a matter of common experience zinc sulphate and hydrogen when mixed do not lead to zinc and sulphuric acid. We would not, ordinarily, write,

$$H_2 + ZnSO_4 = Zn + H_2SO_4$$

This situation is expressed by saying that the reaction is not a reversible one. At any rate it is not reversible under simple conditions.

But there are reactions in which there is a marked degree of reversibility. It is within our common laboratory experience that the two following reactions may be easily brought about:

$$H_2O \rightarrow H_2 + O$$
$$H_2 + O \rightarrow H_2O$$

We express this fact by the additional symbol, $\rightleftarrows$, suggested by van't Hoff, and write

$$H_2 + O \rightleftarrows H_2O$$

In the chapter on hydrogen it was shown that when steam is passed over a hot metal, as iron, the oxide of hydrogen is decomposed, with liberation of the latter element and formation of oxide of iron. This fact is usually illustrated by the equation which follows:

$$4H_2O + 3Fe = 4H_2 + Fe_3O_4$$

But some pages in advance, in the same chapter, an experiment was discussed in which hydrogen passing over a hot metallic oxide decomposes the latter with production of pure metal and water. Oxide of copper was chosen for this illustration, but the iron oxide would have done as well. Attention was called to the seeming contradiction in the two experiments, since for the latter we should write:

$$4H_2 + Fe_3O_4 = 4H_2O + 3Fe$$

Before attempting an explanation of the apparent contradiction a few similar cases must be referred to. It has long been known that when the two common substances alcohol and acetic acid are mixed and allowed to stand the odor of acetic ether, or ethyl acetate, is de-

veloped, showing that the two substances act on each other even without heat. On warming, the action is much hastened but it is not complete; that is, some portion of each of the two substances remains, ordinarily, uncombined. It has been noticed, however, that with increased amount of the alcohol and constant amount of acid the fraction of the latter remaining uncombined grows gradually less. The simple equation expressing the combination of the two substances is this:

$$\underset{46}{C_2H_5OH} + \underset{60}{HC_2H_3O_2} = \underset{88}{C_2H_5C_2H_3O_2} + \underset{18}{H_2O}$$

With the proportions given, 46 alcohol and 60 acid, almost exactly two thirds of the amount taken is converted into the acetate.

But this singular fact, also, has been observed. The ethyl acetate is decomposed by water and if we start with a mixture of 18 parts of water and 88 parts of the acetate we reach finally the same end result that we found in the first case; we find approximately in either case 15.3 parts of alcohol, 20 parts of acetic acid, 58.7 parts of ethyl acetate and 12 parts of water. This appears, therefore, to be a typical *reversible* reaction and a point of equilibrium is reached when the mixture contains the four substances about in the proportion just given. The proper equation to use is, then:

$$C_2H_5OH + HC_2H_3O_2 \rightleftarrows C_2H_5C_2H_3O_2 + H_2O$$

A somewhat similar condition is found in the problem of the action of an acid on the salt of another acid, as, for example, when hydrochloric acid is added to potassium nitrate or nitric acid to potassium chloride. These reactions are reversible, also, and when *molecular* proportions are taken (that is, amounts proportional to the molecular weights) a simple equilibrium point is found. We write, then:

$$HCl + KNO_3 \rightleftarrows KCl + HNO_3$$

Whether we start with hydrochloric acid and potassium nitrate or nitric acid and potassium chloride we find always the four products in the final mixture. With a great excess of one acid or the other, however, the conversion of the salt becomes more and more complete. Many more illustrations might be given but these are sufficient for the present purpose. It is evident that besides "chemical affinity" another factor comes in to modify or change the direction of chemical changes. This factor is that of the *mass* or relative amount of each constituent considered, and even quite early in the history of chemical theory attempts were made to define its value. It remained for the French chemist Berthollet to give tangible expression to an idea which he declared to be of fundamental significance: "Any substance which tends to enter into chemical union exerts an action proportional to its affinity and to its mass." This was written in a work published in 1803, but the importance of the statement, as far as the action of mass is concerned, was lost sight of for many years. Finally two Norwegian investigators, Guldberg and Waage, published a work, in 1867, on the subject of chemical affinity in which the Berthollet idea is fully developed and given a mathematical form. The *mass action law* has become one of the foundation laws of modern chemical theory. A simple illustration of the law may now be given.

Let us consider two molecules, A_1 and A_2, which react on each other to form two new molecules, $\bar{A}_1$ and $\bar{A}_2$, and assume them to exist in a homogeneous mixture. As the intensity or rapidity of the reaction must depend on the frequency with which the molecules may come in contact it is evident that the *concentration*, or number of molecules in a given volume of the reacting mixture, is a determining factor. Representing the concentration of the first by c_1 and of the second by c_2 the product of the two must measure (within certain limits which need not be discussed here) the frequency with which the molecules come into acting contact. In all chemical reactions another factor besides that of the mass enters and this depends on the peculiar nature of the substances themselves.

We may call it the velocity constant, or affinity constant or coefficient, and represent it by the letter k. The velocity of the reaction between A_1 and A_2 may then be formulated in this way:

$$v = kc_1c_2,$$

where k is the measure of the Berthollet affinity and c_1 and c_2 the measure of the masses. When c_1 and c_2 are unity k represents the relative number of molecules reacting or changing.

Now let us assume that the reaction is a reversible one and that A_1 and A_2 have a tendency to go back into A_1 and A_2, that is,

$$A_1 + A_2 \rightleftarrows \bar{A}_1 + \bar{A}_2$$

The velocity of the reaction from right to left may be expressed in a manner analogous to that for the first reaction, thus:

$$v_1 = k_1\bar{c}_1\bar{c}_2$$

When equilibrium is reached it does not follow that no chemical change is taking place: it is altogether likely that chemical changes occur in one direction just as fast as in the other, because the impact of the molecules still goes on, and then $v = v_1$. When this is true

$$kc_1c_2 = k_1c_1c_2$$

At any time before equilibrium is reached the velocity of change in one direction is greater than that in the other. The actual individual velocities cannot be directly observed, but only the excess of one over the other, which may be represented by V. Then,

$$V = v - v_1 = kc_1c_2 - k_1\bar{c}_1\bar{c}_2$$

In the above illustrations it has been assumed that only one molecule of each kind is present; in a more general case we may

consider m molecules of each kind brought into the action and write:

$$m_1A_1 + m_2A_2 + m_3A_3 + \ldots \rightleftarrows n_1\bar{A_1} + n_2\bar{A_2} + n_3A_3 + \ldots$$

The effect of m_1 molecules of A_1 is c_1 raised to the m_1^{th} power, and therefore where we express the velocity equation in terms of the concentrations we must write,

$$kc_1^{m_1}c_2^{m_2}c_3^{m_3}\cdots = k_1\bar{c}_1^{n_1}\bar{c}_2^{n_2}\bar{c}_3^{n_3}\cdots,$$

when equilibrium is reached.

This equation may be transposed to read:

$$K = \frac{k}{k_1} = \frac{\bar{c}_1^{n_1}\bar{c}_2^{n_2}\bar{c}_3^{n_3}\cdots}{c_1^{m_1}c_2^{m_2}c_3^{m_3}\cdots}$$

It must be remembered that the concentration values, c, change from the beginning of the reaction until equilibrium is reached. When this is the case the relation of the reaction velocities becomes a constant which we call K. The equation shows that it is measured by the product of the resultant concentrations of the bodies acting in one direction (and each raised to the power expressing the number of molecules of each substance which act) divided by the product of the concentrations of the bodies acting in the opposite direction (and raised to the proper power as before).

The meaning of these equations may be illustrated by the reaction between alcohol and acetic acid referred to some pages back:

$$C_2H_5OH + HC_2H_3O_2 \rightleftarrows C_2H_5C_2H_3O_2 + H_2O$$

Assume that amounts proportional to 1 molecule of alcohol and acid are mixed; it has been explained that when a condition of equilibrium is reached the mixture contains the four substances in these proportions:

$\frac{1}{3}$ mol. $C_2H_5OH + \frac{1}{3}$ mol. $HC_2H_3O_2 +$
$\frac{2}{3}$ mol. $C_2H_5C_2H_3O_2 + \frac{2}{3}$ mol. H_2O

Assume in another case that we start with 1 mol. of acid and p mols. of alcohol and that x mols. of acid and alcohol are converted. The concentrations depend on the *volume* of the reaction mixture and are expressed by 1/v, etc. When equilibrium is reached these relations obtain, as the reaction takes place between single molecules:

$$k\frac{1-x}{v}\cdot\frac{p-x}{v}=k_1\frac{x}{v}\cdot\frac{x}{v}$$

If the original mixture contains in addition to the acid and alcohol q molecules of water we have this equation:

$$k\frac{1-x}{v}\cdot\frac{p-x}{v}=k_1\frac{x}{v}\cdot\frac{q+x}{v}$$

To find the fundamental relations, however, let us assume the simplest case with $p=1$ and $q=0$. Then $x=\frac{2}{3}$, and we have:

$$\tfrac{1}{9}k=\tfrac{4}{9}k_1 \text{ or } k=4k_1$$

If we substitute these values in the above equations, leaving $q=0$, and solve the equation for x we find,

$$x=\tfrac{2}{3}(p+1-\sqrt{p^2-p+1})$$

In other words, in mixtures in which the acid is constant and the alcohol is taken in varying amounts the extent of decomposition, x, depends on the alcohol value p, expressed in molecules. Actual experiment shows a result agreeing very well with the theory. In a certain series of experiments when p was taken as 8 molecules the value of x, or acid combined, was found to be 0.945 while the formula above calls for 0.966. In another series of experiments reported, with $p=2$, the value of x was found as 0.858, while the formula calls for 0.845. In cases where a large excess of alcohol is used the combination of the acid is still more complete. These observations illustrate very well what is known as the effect of mass on the reaction.

Another illustration may be given here, drawn from a reaction referred to in the chapter on iodine. Attention was there called to the reversible reaction:

$$2HI \rightleftarrows H_2 + I_2$$

At the ordinary temperature the reaction is very slow but at the temperature of boiling sulphur the union of hydrogen and iodine on the one hand, or the decomposition of hydriodic acid on the other may be easily followed. The same equilibrium composition is soon reached whether we start with the two elements or the compound gas. Using the symbols employed before we have in equilibrium,

$$kc^2 = k_1c_1c_2$$

$$K = \frac{k}{k_1} = \frac{c_1c_2}{c^2}$$

In such gas reactions in place of the concentrations we may use the *partial pressures*, that is the fractions of the whole gas pressure due to each component of the mixture. Then we have

$$K = \frac{P_1P_2}{p^2}$$

In certain series of experiments reported it has been found that for every 1000 molecules of hydrogen involved in the reaction about 225 are left free when the condition of equilibrium is reached, the iodine being present in the same proportion. This would lead to the following expression for the composition of the mixture:

$$1550HI + 225H_2 + 225I_2$$

To reach the general formula assume the hydrogen originally present as uncombined and $= 1$, the iodine $= a$ and the hydriodic acid, when equilibrium is reached, $= 2x$. Then

$$K = \frac{P_1P_2}{p^2} = \frac{(1-x)(a-x)}{4x^2}$$

Taking a as equivalent exactly to the hydrogen we have, using the above numerical values,

$$\frac{k}{k_1} = K = \frac{(1-x)^2}{4x^2} = \frac{.225^2}{4 \times .775^2} = .021$$

This means that the velocity coefficient of the reaction in one direction is about 50 times as great as in the other.

With K determined, the value of x for any value of a (the amount of iodine for unit value of hydrogen) may be found by solving the above general equation. We have,

$$2x = \frac{1 + a - \sqrt{1 + a^2 - a(2 - 16K)}}{1 - 4K}$$

$$2x = \frac{1 + a - \sqrt{1 + a^2 - 1.66a}}{0.916}$$

The following table illustrates the use of the last formula. In some experiments published a few years ago definite quantities of iodine and hydrogen were allowed to act on each other at a temperature high enough to quickly bring about equilibrium. The amount of hydriodic acid formed was measured in each case. In the first and second columns of the table we have the actual volumes of hydrogen and iodine used, in the third the iodine volume corresponding to H = 1, or a of the above formula. In the fourth column we have the hydriodic acid, or the calculated 2x of the above formula, based on the value H = 1. In the fifth column we have the acid values corresponding to the amount of H as given in column 1. Finally, in the last column there are given the amounts of hydriodic acid as actually found by experiment.

H_2 Cc.	I_2 Cc.	a, or I value for H = 1.	HI, or 2x of the above formula.	HI for H of column 1.	HI as found
8.10	2.94	0.363	0.696	5.64	5.66
7.94	5.30	0.668	1.195	9.49	9.52
8.07	9.27	1.149	1.669	13.47	13.34
8.12	14.44	1.780	1.839	14.93	14.82
8.02	27.53	3.433	1.939	15.54	15.40
7.89	33.10	4.195	1.952	15.40	15.12

In these figures the very good agreement between the theory and the actual observations will be noted. For the same value of hydrogen, but increased iodine there is a gradual increase in the hydriodic acid found, which is best shown in the fourth column. The last numbers there given for the acid reach nearly the maximum possible, which is 2 Cc. for 1 Cc. of hydrogen. The reason for this will appear in a later chapter. In general, the results of the experiments agree with those on the union of alcohol and acetic acid where increase of mass of one of the components of the mixture brought about a nearly perfect combination of the other.

We are now able to take up the reversible reaction which has been referred to several times:

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2$$

As the experiments were carried out it would not be possible to find a point of equilibrium, if one really exists. In one case the steam was in very great excess and the hydrogen formed was rapidly swept out of the tube; it had therefore no opportunity to start an appreciable reaction in the opposite direction. In other words, the relative mass of the hydrogen was small. In the second case hydrogen was kept in great excess and this had the effect of conducting off the water vapor as fast as liberated; this is equivalent to saying that the mass of the vapor is maintained relatively very small, making a reverse reaction practically impossible.

But the experiments have been made in such a manner as to show the four substances in equilibrium, and this has been accomplished by starting in one case with a tube filled with finely divided iron, exhausting the air and saturating the space left with water vapor maintained at a known tension. In another case a tube containing iron oxide was swept through with hydrogen to expel air. Each tube was so arranged that it could be heated to a definite temperature, in the vapor of boiling mercury or boiling sulphur for example, and at one end each was connected with a manometer to measure pressure and at the other with a small flask containing water at a low temperature from which the tensions of the aqueous vapor concerned in the reaction could be accurately determined. (Experiment of Deville.)

Now, starting with either combination, iron and aqueous vapor, or iron oxide and hydrogen, it was found that at a given temperature when the point of equilibrium was reached, as shown by the manometer, the relation of the gas to the vapor became the same from either direction. At a temperature of 860° the combination $3Fe + 4H_2O \rightarrow$ led to equilibrium when the partial pressures (tensions) of the hydrogen and water vapor

were respectively 12.8 and 4.6. That is, $H/H_2O = 2.783$. At the same temperature the combination $Fe_3O_4 + 4H_2 \rightarrow$ led gradually to the same partial pressures.

The following short table from Deville's results will show the values actually obtained in experiments at different temperatures in the reaction $3Fe + 4H_2O \rightarrow$. W and W_1 represent partial pressures of the water vapor observed, H and H_1 corresponding partial pressures of the hydrogen liberated when equilibrium was reached.

Temp.	W	W_1	H	H_1	$r = \frac{H}{W}$	$r_1 = \frac{H_1}{W_1}$	$R = \frac{r_1}{r}$
200°	4.6	9.7	95.9	195.3	20.85	20.13	0.97
265°	4.6	15.7	64.2	235.1	13.96	14.97	1.07
360°	4.6	9.5	40.4	76.3	8.78	8.03	0.91
440°	4.6	10.1	25.8	57.9	5.61	5.73	1.02

Coming back to the equation and recalling the general formulas used we have

$$\underset{P}{3Fe} + \underset{p^4}{4H_2O} \leftrightarrows \underset{P_1}{Fe_3O_4} + \underset{p_1^4}{4H_2}$$

where P and P_1 may be taken as representing the active masses of the solids in the reaction. Then

$$kPp^4 = k_1P_1p_1^4$$

$$K = \frac{k}{k_1} = \frac{P_1}{P} \cdot \frac{p_1^4}{p^4}$$

It has been shown that in such combinations the masses of the *solids* may be considered as constant and so dropped from the right hand member of the equation. There remain then the partial pressures of the hydrogen and water vapor and the quotient of one by the other should be constant at any given temperature. This is shown by the above table where K is represented by the quotients H/W and H_1/W_1, which are nearly the same. Such experiments are very difficult, but the values in the last column, R, show how near constancy is approached at different temperatures.

In the above discussion it is important to note the change in K with the temperature. At the lowest temperature equilibrium is reached with the hydrogen greatly in excess, and the constant is 20.5 in the mean.

But with elevation of temperature the reaction favors the formation of water and the constant sinks now to 5.67 at 440°, 2.78 at 860° and about 1.0 at 1600°. In all such reactions, then, it must be remembered that temperature, as well as the masses concerned, plays a very important part.

It is also true, and this applies to all equilibria reactions, that if a product may be removed as fast as formed a total change in its favor may be accomplished, even if the product is formed only in traces. In the reduction of iron or copper oxide in the one case and the decomposition of water by iron in the other the products, water and hydrogen, may be swept out as fast as formed, as shown by the experiments given in an earlier chapter. In the experiment on the reduction of copper oxide it was very easy to completely reduce the oxide by using excess of hydrogen.

In the work which is to follow we shall have frequent occasion to come back to the subject of reversible reactions and conditions of equilibrium and to point out how important these considerations are for the proper understanding of many familiar phenomena. In many practical cases simple reactions obtain which may be expressed by formulas involving four molecules:

$$A + B \rightleftarrows C + D$$

What actually takes place depends largely on the concentration, and we use the symbols C_A, C_B, etc., to express the concentrations in which these several bodies are present. We have then,

$$\frac{C_A \times C_B}{C_C \times C_D} = K$$

as a common form of expressing the general relations. This may be expressed by saying that in a reversible reaction the product of the concentrations of the first set of bodies must bear a constant relation to the product of

the concentrations of the second set of bodies when equilibrium is reached.

THE NATURE OF SOLUTIONS.

In the preceding pages the term *solution* has been frequently used but as yet no theory has been given as to the composition of these mixtures. At one time this was supposed to be a very simple matter, but with advance of knowledge our ideas have materially changed and just what the condition in a solution actually is may not be readily explained.

According to the older notions a solution of salt in water consisted of a perfectly homogeneous mixture of individual water molecules, H_2O, and individual salt molecules, NaCl. In the one case the hydrogen and oxygen atoms were supposed to be very firmly united to each other and in the second case the sodium and chlorine were assumed to be permanently united. It was held that to decompose the one molecule or the other a very strong force was necessary, or the action of some chemical substance with great "affinities." Sulphuric acid was said to decompose salt because of its greater affinity for sodium than that possessed by hydrochloric acid:

$$H_2SO_4 + 2NaCl = Na_2SO_4 + 2HCl$$

But many phenomena became in time known which gradually led to the belief that the union between such elements as sodium and chlorine, or potassium and the NO_3 group in saltpeter, is a very loose one as these salts exist in solution. Suppose, for example, that we lead an electric current through a solution of silver nitrate between plates of silver or through a solution of copper sulphate between plates of copper; according to the older notion a current to pass at all must have an electromotive force great enough to overcome the *affinities* between the metals and their combined acids. But as a matter of fact the weakest possible electromotive force has been found sufficient for this purpose, and silver is carried in the one case and copper in the other to the proper kathode. The

two metals behave as if they were already free and ready to be transported. Various other phenomena of electrical conductivity lead to the same notion. In addition, a study of the freezing point, or boiling point, of salt solutions, or of solutions of acids and bases suggests very strongly that in these classes of compounds the component atoms or groups are not firmly held together, but are in part *dissociated* or separate. Most of these phenomena are too complicated to be discussed at this point, but it may be said that as a result of many studies chemists have come to about this idea of the condition of acid, base or salt molecules in aqueous solution. In regard to other than water solutions our conceptions are much less definite.

It must be explained, however, that the notion of dissociation is but a working hypothesis which is convenient because of the large number of phenomena which it correlates. Of all the modern theories on the nature of solutions it is the most fully developed. Other views will be referred to in a later chapter when salts are more particularly discussed. As our knowledge of solutions other than aqueous solutions increases the difficulties in the way of framing a simple tangible theory of the nature of solutions in general appear to grow greater rather than less.

Ionic Dissociation. In going into solution in water the important classes of molecules just mentioned, that is the acids, bases and salts, split up more or less completely, it is held, into their component parts or groups called *ions*, following the name suggested by Faraday. These ions may be the atoms of binary compounds, or such groups as OH, NO_3 or SO_4 from more complex bodies. Water is said to have the power of *dissociating* these molecules but just what the mechanism of this dissociation is we do not know. Sodium chloride in dissolving in water furnishes ions of chlorine and sodium, which exist side by side. These ions are the free atoms, apparently, but they differ immensely from the ordinary sodium and chlorine which we are familiar with. One atom seems to possess a very powerful charge of positive

electricity and the other an equally strong charge of negative electricity by virtue of which they remain free in solution. When these atoms are thrown out of solution, as is the case during electrolysis, the charges of electricity are lost and the ordinary chemical molecules result. Just where the ions secure their electric charges originally is not easily explained; it is likely that the dissolved molecule contains the two charges in balanced or saturating condition and the function of the solvent is to separate the component atoms, or groups, one of which carries the positive charge and the other the negative. The power of *dissociating* ordinary molecules is found in solvent liquids in very different degrees; in water it is very great, while in some other liquids it is small. The reason for this is not known.

The extent of dissociation depends on the strength of the solution in question, and also on the nature of the dissolved substance. In general it is true that the dissociation increases with the dilution; that is, in dilute solutions of acids, bases and salts the number of molecules broken up into ions is greater than in concentrated solutions. Indeed, in some concentrated solutions the degree of *ionization* appears to be quite small. The power of conducting the electric current seems to depend largely, in the case of solutions, on the number of ions present in a given volume, and it has been found that some strong solutions have, both absolutely and relatively, a lower conducting power than that possessed by weaker solutions of the same substances.

It must be explained here that many common substances do not appear to be separable into ions. This is true of ether, alcohol, chloroform, the hydrocarbons, the sugars and a very large number of other *organic* compounds about which more will be said in the proper place. All these bodies are *non-electrolytes*, that is, they do not conduct the electric current. In addition to this they are not active in the ordinary chemical sense. Chloroform may be taken as an illustration. This substance contains chlorine, but the usual tests for chlorine as given in an earlier chapter are wholly lacking. The ordinary re-

actions of inorganic chemistry are believed to be ion reactions; those bodies which are not dissociated, and which in consequence do not conduct the electric current when in solution, fail also to enter into chemical combinations or yield precipitates in the usual way.

This notion of ions as the active element in chemical changes offers a tangible explanation of many obscure reactions; a few of the more important deductions from the theory will therefore be given here. We may take first a simple typical reaction to illustrate some points:

$$NaCl = \overset{+}{N}a + \bar{C}l$$

This equation implies that sodium chloride separates into the positive and negative ions, Na and Cl. This change is brought about usually in solution, but, as suggested above, the dissociation is not complete except in very dilute solutions. In stronger solutions we have undissociated molecules and the ions, side by side. Therefore in concentrating a weak solution the change would follow in the opposite direction. The reaction appears then as a reversible one and must be written:

$$NaCl \rightleftarrows \overset{+}{N}a + \bar{C}l$$

A point of equilibrium exists somewhere and this must vary with the concentration of the interacting components. Employing the letter C to represent concentration we may follow the method explained above in illustrating the mass action law and write:

$$\frac{C_{\overset{+}{N}a} \times C_{\bar{C}l}}{C_{NaCl}} = K, \text{ or constant}$$

Now, assuming the truth of this general formula let us notice what must happen on changing the concentration, by evaporation, for example. If half the water be driven off it might appear that all the concentrations would be just doubled. But this can not be the case, for if we

double Na and $\bar{C}l$ the numerator product would be increased four times while the denominator would be increased but twice. The quotient, or K, would therefore cease to be constant. To maintain the constant ratio some of the ions must unite to form NaCl. The product of $C_{\dot{N}a}$ and $C_{\bar{C}l}$ would be less than the quadruple value while C_{NaCl} would be more than double in value. Unfortunately the methods employed in finding numerical values for K are somewhat complex and can not be explained here.

In like manner, granting the applicability of the above formula, it would follow that the addition of a substance containing a sodium or a chlorine ion to the sodium chloride solution must decrease the dissociation of the last named salt. For example, the addition of hydrochloric acid to a solution of common salt results in a concentration of the undissociated NaCl, and this may even extend to the precipitation of some of the salt. If we consider a saturated solution of a salt we must still have some degree of dissociation; the extent of solubility bears a peculiar relation to the numerator of the above general formula, since if we increase the product of the numerator terms, part of the substance represented by the denominator must go out of solution to maintain the constant value of K.

Experiment 104. To illustrate these points some simple experiments may be made.

Prepare a saturated solution of common salt and filter if not clear. To about 10 cubic centimeters of this solution add a few drops of strong hydrochloric acid solution and note that a little of the salt separates. A like separation does not follow on adding nitric acid.

Prepare a saturated solution of potassium chlorate and add to a little of it a few drops of concentrated solution of potassium chloride. A precipitate of chlorate soon settles. The addition of sodium chlorate causes a like separation of potassium chlorate.

Solubility Product. This term is applied to that product of the ion concentrations which cannot be exceeded without throwing some of the dissolved salt out of solution. In a saturated solution containing some undis-

solved salt in suspension, or in a solution over undissolved salt the solubility product must be a constant. In the study of qualitative analysis numerous illustrations of the importance of these principles are found, and in later chapters of this book more references will be made to them.

Acids, Bases, Salts. Inorganic chemistry is concerned largely with a study of these compounds. The common acids are dissociated in aqueous solution more or less completely, the degree of dissociation increasing with the dilution. The acid property appears to be due to free hydrogen ions. Hydrochloric, nitric and sulphuric acids are called *strong* acids, because they furnish many free ions when dissolved. They are good conductors of the electric current in this condition, but free from water they are not.

The ordinary bases which we are acquainted with in inorganic chemistry are hydroxyl bodies. Potassium hydroxide, sodium hydroxide and ammonium hydroxide are good illustrations. Their important properties will be discussed later. These bodies in aqueous solution are dissociated, the first two strongly and the last much less. The hydroxyl group, OH, is the characteristic of these compounds and the basic reaction is due to this group as an ion.

Salts are formed by the union of acids and bases. The common inorganic salts are readily dissociated in aqueous solution. The reaction of many of these solutions is neutral, but in other cases acid or alkaline reaction may be observed, and the reasons for this will be pointed out later. The neutral reaction is found when the salt is formed by the combination of a strong acid with a strong base. We have a good illustration of this in common salt, which may be looked upon as formed in this way:

$$NaOH + HCl = NaCl + H_2O$$

If this is written to show the dissociated condition we have:

$$\overset{+}{N}a,\ \overset{-}{O}H + \overset{+}{H},\ \overset{-}{C}l = \overset{+}{N}a,\ \overset{-}{C}l + H_2O$$

The water formed is not dissociated to any appreciable extent. All of these points will receive fuller discussion in a following chapter.

Osmotic Pressure of Solutions. When substances dissolve in water or other liquids a further interesting phenomenon is observed. The dissolved particles distribute themselves among the liquid particles and exhibit there a very peculiar pressure which is distinct from the pressure of the liquid as a whole on the walls of the containing vessel. This pressure is known as *osmotic pressure*. The dissolved molecules behave very much as *gases* would in the same space, free from liquid. Two grams of hydrogen (one molecule weight), condensed to one liter, would exert a pressure of about 22 atmospheres. The molecular weight of sugar, expressed in grams, dissolved in water to make a liter of solution has been found to exert practically the same pressure when observed in proper apparatus. This appears to be true of molecules in general, that is, they exert the same pressure that an equal number of gaseous molecules would in the same space, but in the case of electrolytes the pressures are abnormally large which suggests, again, ionic dissociation, and the independent action of the ions. Further than this the osmotic pressure of dissolved substances increases with the temperature, and apparently at the rate which is known to be true for gases. In general, in other words, solids dissolved to form solutions in water seem to obey the gas laws, already referred to. It is proper to add, however, that many chemists fail to recognize this perfect parallelism, and give other interpretations of the phenomena.

Ind. Feb 21 - 7100 P.M.

CHAPTER VIII.

SULPHUR AND ITS COMPOUNDS, SELENIUM AND TELLURIUM.

Sulphur is an element which occurs abundantly in nature in the free state and in many sulphides and sulphates. It is widely distributed.

Preparation. Crude native sulphur occurs in Sicily in large quantities and is refined by very simple processes. Sulphur melts at a relatively low temperature and the first refining consists in melting it away from the accompanying earthy materials. The crude ore is heaped up in a large pit dug in a hillside and ignited. The combustion of a part of the sulphur furnishes heat enough to melt the rest which collects at the bottom of the pit and then escapes through an opening leading to a lower reservoir. The product so obtained is not pure but may be refined by distillation from large retorts.

Some sulphur is obtained by distillation of certain sulphide ores containing it, but the amount so produced is not important. At a high heat a sulphide of iron decomposes as here represented:

$$3FeS_2 = Fe_3S_4 + S_2$$

That is, one third of the total sulphur may be obtained in the free state. It will be recalled that the dioxide of manganese may be broken up in the same manner:

$$3MnO_2 = Mn_3O_4 + O_2$$

Vast quantities of sulphur exist in deposits occurring in southern Louisiana, at a considerable depth below the surface of the earth. After many futile attempts to mine this, it has recently been found possible to bring it to the

top of the ground in this manner: Holes are bored down to the deposit, and these are doubly piped. A large pipe fills the boring, and inside of this a smaller one goes down to a somewhat greater depth. Hot water under great pressure and at a high temperature, about 170° C., is pumped down in the space between the pipes. This melts the sulphur in the deposit and ultimately forces it up through the inner pipe. To aid in maintaining a high temperature, a third small pipe passes down through the one which conveys the sulphur to the surface. A current of hot air is forced down in this, but the pressure on it is less than that on the water. The molten sulphur on reaching the surface is run into shallow pans to cool and solidify. It is nearly pure, and for most purposes needs no refining.

Properties of Sulphur. Sulphur appears in commerce in fine powder or "flowers of sulphur," and as roll sulphur or "brimstone." Both varieties are insoluble in water, but soluble in carbon disulphide, and in several other liquids. The solubility in carbon disulphide may be shown by experiment.

Experiment 105. Take about 10 Cc. of carbon disulphide in a test-tube and add 3 or 4 grams of the fine sulphur. Shake the tube until all dissolves, then pour the solution into a small beaker, which leave in a quiet place for spontaneous evaporation. The sulphur separates in octahedral crystals.

Sulphur melts at a temperature of about 115° C. to a thin yellow liquid; at a higher temperature it grows darker and becomes viscid, so that it can be poured only with difficulty. This and other facts may be readily shown by trial. The boiling point is about 448°. Sulphur crystallizes in several forms which exhibit different physical properties. A form which crystallizes in octahedra is found in nature. Similar rhombic octahedra are obtained by crystallization from carbon disulphide as explained above. These crystals have a specific gravity of 2.05 at 0°. When sulphur is melted and allowed to cool slowly, a portion of it separates in long needles of the monoclinic system. These have a lower specific

gravity than the octahedral variety, viz.: 1.96. These monoclinic prismatic needles may be easily obtained by melting some sulphur in a test-tube and allowing it to cool a short time until a solid crust forms over the top. When this is broken through, the still liquid portion may be poured out, leaving a crystalline mass attached to the sides of the tube.

Experiment 106. Melt 15 to 20 Gm. of sulphur in a test-tube slowly and observe the changes in color and degree of fluidity. Above about 250° C. the melted mass grows thinner. After it has become quite thin pour it into some water and allow it to cool. A stringy plastic mass is obtained which is elastic like crude rubber. Set this aside and allow it to remain several days, and then observe that it has become brittle, or has returned to the common form.

At the ordinary temperature the affinity of sulphur for the metals is slight, but at higher temperatures many combinations may be easily made. It has been shown already that sulphur and copper unite very readily when strongly heated. The same reaction will now be shown with iron.

Experiment 107. In a test-tube mix some flowers of sulphur with about an equal weight of finely divided iron. Fine filings or powder are preferable, drillings being usually too coarse. Heat the mixture slowly in the lamp flame. The sulphur melts and finally reaches a temperature at which chemical union between the two substances, accompanied by glowing of the mass, takes place. The iron burns with the sulphur as it does in oxygen and the product is sulphide of iron, or ferrous sulphide. When the tube cools, break it, and examine the contents. Powder some in a mortar and observe the uniform dark color. Put some small pieces in a test-tube, add some water and then a little hydrochloric acid. Observe that a gas with a very disagreeable odor is given off.

Uses of Sulphur. Sulphur is employed in the manufacture of sulphuric acid, in gunpowder (ordinarily a mixture of sulphur, saltpeter and charcoal), in many varieties of friction matches and in the preparation of several sulphides. It is employed in considerable quantity in the vulcanization of rubber and in the preparation of so-called hard rubber. It has also numerous minor applications, in medicine and in the arts.

SULPHUR AND OXYGEN.

Sulphur forms two important compounds with oxygen, one of which has been referred to before in the experiments on oxygen gas. At a temperature sufficiently elevated the union takes place directly as has been shown. The product formed is sulphurous oxide, SO_2.

Sulphurous Oxide. This oxide is found to a small extent in the atmosphere of cities where much soft coal is burned. It is also given off in some volcanic gases. For experimental purposes it may be obtained by a peculiar reaction in which copper is made to decompose strong sulphuric acid, as explained below.

Experiment 108. Arrange apparatus as shown in the illustration. The flask should hold 400 to 500 Cc. Put in it 15 to 20 Gm. of copper in small pieces or turnings and add 25 Cc. of strong sulphuric acid. The Woulfe bottle contains a small amount

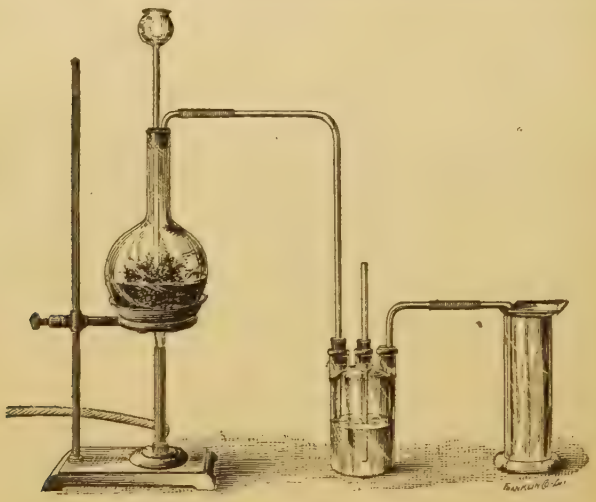


FIG. 17.

of water to wash the gas passing through it, and the delivery tube from this can be led into another vessel of water, or into

a clean dry bottle, for collection of the gas. Apply heat to the flask and when gas bubbles begin to escape rapidly, lower the flame to avoid too violent a reaction. Collect first several bottles of the gas, by displacement of air, which can be easily done as the gas is over twice as heavy as air. In collecting the gas cover the dry bottle as well as possible with a glass plate or perforated cardboard. When the bottle is full a burning match held at the mouth will be extinguished. As the bottles fill cover them and set aside for experiment. Then lead the delivery tube into a bottle of water and allow this to stand as long as gas is given off. The water absorbs the gas and is used below.

For technical purposes sulphurous oxide may be made by heating charcoal with strong sulphuric acid. A reduction of the acid takes place and oxide of carbon is formed as well as oxide of sulphur:

$$C + 2H_2SO_4 = CO_2 + 2H_2O + 2SO_2$$

For operations on the large scale, such as bleaching and fumigation, the oxide is made by burning sulphur in the air or by roasting certain sulphides called *pyrites*.

Properties of Sulphurous Oxide. Of these, the odor is most characteristic, while in its chemical behavior several marked peculiarities may be easily shown. In collecting the gas the fact that it is not a supporter of combustion was shown. That sulphurous oxide is a good bleaching agent can be shown by experiments on printed cotton goods.

At a low temperature the gas may readily be condensed to the liquid condition. The boiling point of the liquid is $-8°$, and in this form it is an article of commerce, being employed in refrigeration.

Experiment 109. Moisten a strip of calico and suspend it in a bottle of the gas, allowing it to remain half an hour. Many colors are completely bleached in this time. It must be noted, however, that some colors are not at all acted upon by the gas, and many of those which seem to be destroyed return after a time. The action of the gas is much less destructive than is that of chlorine.

Experiment 110. The marked solubility of sulphurous oxide in water may be shown by means of a bottle well filled by the gas. Invert the bottle, closed by a glass plate, bring the mouth be-

neath the surface of water and then remove the plate. Water rushes up to take the place of the dissolved gas, as was the case in the experiment with ammonia. Lift up the bottle by means of the plate and observe that the water has an acid reaction, as shown by the litmus paper test.

At a temperature of 0° 1 volume of water dissolves nearly 80 volumes of the gas; at 20° 1 volume of water dissolves 39.5 volumes of the gas; one liter of the gas weighs 2.89 gm. at 0°.

Experiment 111. Moisten a long splinter of pine wood in strong nitric acid and dip it into a bottle of the gas. Red fumes are formed of oxides of nitrogen, showing the decomposition of the nitric acid. In this reaction the sulphurous oxide is said to act as a *reducing* agent. The meaning of this term will be explained below.

We have remaining the solution of the gas in water, obtained by direct absorption. Tests may be made with it as follows:

Experiment 112. Pour portions of about 10 Cc. each into several test-tubes. To one add some solution of potassium permanganate, a few drops at a time. The deep purple color of this solution gives place to a very light pink. Into another portion pour a few cubic centimeters of a dilute solution of potassium dichromate. Notice the change of color to green. Boil a few cubic centimeters of ferric chloride in a test-tube and pour this, a few drops at a time, into the solution of sulphurous oxide, heating the latter after each addition. The yellowish brown color of the iron solution changes to pale green by this treatment. These are all reduction actions again.

Experiment 113. Pour about 10 Cc. of the sulphurous oxide solution into a porcelain dish, which place on a sand-bath and heat. Everything evaporates, showing that the product is volatile The solution is called sulphurous acid, but, like the ammonium hydroxide, is not stable. In another dish pour about 25 Cc. of the solution, add to it some litmus, and then dilute solution of caustic soda until the color turns blue. Then restore the red color by addition of more sulphurous oxide solution, put the dish on a sand-bath, and evaporate slowly to dryness. A white residue is left which has a sharp saline taste, quite distinct from that of the caustic soda. Now add a little water to the dish and some dilute hydrochloric acid. Effervescence follows with escape of gas, which the odor shows is sulphurous oxide. The caustic soda formed with the solution sodium sulphite, which is decomposed by the hydrochloric acid, with liberation of the sulphurous oxide and formation of sodium chloride.

Experiment 114. Pour 10 Cc. of the fresh sulphurous oxide solution into a test-tube and add to it a few drops of solution of barium chloride. A precipitate forms which consists of barium *sulphite*, and which dissolves readily by addition of a little hydrochloric acid. Now repeat the experiment, but add two or three drops of strong nitric acid to the sulphurous oxide solution, boil a few minutes and complete as before. A white precipitate forms here which does not dissolve on addition of hydrochloric acid. This is barium *sulphate*.

Leave the bottle containing the remainder of the sulphurous oxide solution uncorked, but away from dust, for future experiments.

We must now turn to a consideration of the chemical changes involved in the experiments above. First, we have the reaction by which the sulphurous oxide was produced. When copper dissolves in hot sulphuric acid copper sulphate is formed, while water vapor and the sulphurous oxide are given off. Sulphuric acid contains, as already shown, hydrogen, oxygen and sulphur in the proportions given by the formula H_2SO_4. The liberation of the sulphurous oxide, therefore, involves the breaking up of this group. It is possible that we have first a reaction analogous to one which was suggested as taking place between copper and nitric acid, viz.:

$$Cu + H_2SO_4 = CuSO_4 + H_2,$$

and that the liberated hydrogen acts here, as there, as a *reducing* agent; that is, one which decomposes because of its power of combining with oxygen. The second reaction, then, would be this:

$$\underset{\text{Hydrogen}}{H_2} + \underset{\substack{\text{Sulphuric}\\\text{acid}}}{H_2SO_4} = \underset{\text{Water}}{2H_2O} + \underset{\substack{\text{Sulphurous}\\\text{oxide}}}{SO_2}$$

If we consider these two reactions as taking place together we may write:

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$$

It appears from this last equation, which represents the results of experiments made quantitatively, that one

half of the sulphuric acid which takes part in the reaction becomes combined to form a sulphate, while the other half is broken up, yielding water and sulphurous oxide.

Another explanation of the reaction between copper and sulphuric acid has been proposed and is illustrated by these equations:

$$Cu + H_2SO_4 = CuO + H_2SO_3,$$

copper oxide and sulphurous acid being formed. The first dissolves in the excess of sulphuric acid:

$$CuO + H_2SO_4 = CuSO_4 + H_2O,$$

and the second breaks up into water and sulphurous oxide:

$$H_2SO_3 = H_2O + SO_2$$

The experiments made with the sulphurous oxide in the condition of gas or in solution are mainly illustrative of one thing, viz., its reducing or oxygen absorbing power. In the experiment in which a splinter moistened with nitric acid was dipped into a jar of the gas it was observed that reddish fumes were given off. Now, it has been already explained that the appearance of these reddish fumes in reactions in which nitric acid is concerned is indicative of a decomposition of the acid by some substance which can take oxygen. The reddish fumes come from the residue left after this breaking up of the nitric acid. Sulphurous oxide, SO_2, has a great tendency to take up oxygen and form a body called sulphuric oxide, SO_3, and especially in presence of moisture. The nitric acid here furnishes the oxygen for the purpose.

It was shown that the deep purple solution of potassium permanganate is completely decolorized by the solution of sulphurous oxide. The reaction here is somewhat complicated, but is one in which the potassium permanganate parts with oxygen, converting the sulphurous oxide and water into sulphuric acid. The solution of

the potassium dichromate, used in the same experiment, behaves quite in the same manner. The potassium dichromate acts here as an oxidizing agent. Because of their complexity these reactions will not be further explained here, but they are important ones and will be taken up later.

We have next a case which is somewhat simpler. The solution of sulphurous oxide when treated with nitric acid forms sulphuric acid. We know this because after the mixing of the liquids we are able to prove the presence of sulphuric acid by a reaction which will later be shown to be a certain *test* for the acid. What the experiment, carried out in detail, shows to take place is illustrated by this equation:

$$2SO_2 + H_2O + 2HNO_3 = 2H_2SO_4 + N_2O_3$$

That is, an oxide of nitrogen and sulphuric acid are formed.

In the last experiment made it was directed to allow a solution of sulphurous oxide in water to stand exposed to the air. This solution is often considered as one of sulphurous acid, formed by direct union of the substances, thus:

$$SO_2 + H_2O = H_2SO_3$$

After standing some days or weeks exposed to the air we observe that a change has taken place in the liquid. We find that sulphuric acid is present, as we have tests by which we may readily distinguish sulphuric acid from sulphurous. The latter acid takes up oxygen in this manner:

$$H_2SO_3 + O = H_2SO_4$$

Sulphuric acid is formed, therefore, as an oxidation product of sulphurous acid. This leads to the more detailed consideration of the properties of sulphuric acid, given later.

SULPHUROUS ACID AND SULPHITES.

As suggested above and as indicated by experiment, the solution of SO_2 in water may be considered as sulphurous acid. As shown, the acid is not stable but decomposes by heat and on exposure to the air. The sulphites are more stable and several are in common use. The following equation illustrates their formation:

$$2NaOH + H_2SO_3 = Na_2SO_3 + 2H_2O$$

When exposed to moist air most of the sulphites become sulphates by absorption of oxygen.

Uses of Sulphurous Oxide and Acid. It will be shown later that large quantities of sulphurous oxide are made as a step in the manufacture of sulphuric acid. It is also employed in bleaching silk, woolen and straw articles and in the fumigation of buildings. It is used also to protect trees and vines from the ravages of certain pests. Strong solutions of sulphurous acid or of acid sulphites are employed in washing barrels and tanks or vats used in the manufacture and storage of beer. It acts here to destroy ferments, whose presence might spoil the product. In the laboratory a solution of sulphurous acid is often employed as a reagent.

Sulphurous acid is a very weak acid as shown by various phenomena. As there are two hydrogen atoms in the molecule two classes of salts are formed, the *neutral* salts and the *acid* salts. The so-called neutral salts possess, however, an alkaline reaction, which on the dissociation theory is interpreted in this way. In presence of water such salts of weak acids suffer "hydrolysis," that is, they break up, in part, according to this reaction

$$Na_2SO_3 + H_2O = NaHSO_3 + NaOH$$

or,

$$\overset{+}{Na}_2,\ S\overset{-}{O}_3 + H_2O = \overset{+}{Na},\ \overset{-}{OH} + \overset{+}{Na},\ HSO_3$$

The hydroxyl group gives the alkaline reaction, while the group HSO_3 is not further dissociated, or but slightly.

Hyposulphurous Acid. By the action of zinc on a solution of sulphurous oxide a peculiar acid is formed which is the true hyposulphurous acid.

$$Zn + H_2O + 2SO_2 = \underset{\text{Zinc sulphite}}{ZnSO_3} + \underset{\text{Hyposulphurous acid}}{H_2SO_2}$$

The acid forms a yellow solution which absorbs oxygen readily and therefore acts as a strong reducing and bleaching agent. A corresponding salt is made by action of zinc on a solution of sodium acid sulphite:

$$Zn + 3NaHSO_3 = NaHSO_2 + Na_2SO_3 + ZnSO_3 + H_2O$$

The zinc and sodium sulphites may be crystallized out, leaving a solution of the acid hyposulphite which is sometimes used in bleaching. It has been used in the bleaching of syrups and other articles of food, but for this purpose its employment should be strongly condemned.

Sulphuric Oxide or Sulphur Trioxide. This is a substance having the formula SO_3, and is solid at the ordinary temperature. It may be made by several reactions, and readily when a mixture of sulphurous oxide and oxygen gas is passed over hot platinum sponge. This spongy material at a moderate temperature causes the two gases to combine. It may be more easily made by the distillation of a liquid known as fuming sulphuric acid, which will be described below. This acid has the composition $H_2S_2O_7$, and when distilled decomposes forming H_2SO_4 and SO_3, the latter of which may be collected in a cool and perfectly dry receiver.

Properties of Sulphur Trioxide. The substance made as described above appears in the form of dense, white fumes which yield long, silky needles on cooling. This crystalline solid must be preserved in sealed glass vessels. If brought in contact with the air it immediately attracts moisture and becomes liquid sulphuric acid:

$$SO_3 + H_2O = H_2SO_4$$

The trioxide itself melts at a temperature of 16° to form a colorless liquid. In dry form it is without action on litmus paper.

SULPHURIC ACID.

History. This very important acid has been known for many years, and was first made by the distillation of effloresced green vitriol, hence the name, *oil of vitriol,* which still clings to it. Reference to the acid appears first in the writings of the Arabian philosopher Geber, and later, but very indefinitely, in the works of the earlier alchemists. In the fifteenth century Basil Valentine described more clearly the preparation of the vitriol and the distillation of the same. Practically all the acid used for 300 years was made by that reaction which will be referred to again, below. About the middle of the eighteenth century a process was discovered by which sulphuric acid may be made by the oxidation of sulphurous oxide. This process was developed in England, while the other grew to importance in Germany. Much of the common sulphuric acid used to-day is made by a process which is a development of the crude attempts first made in England about 150 years ago.

Preparation. The manufacture of sulphuric acid on the large scale involves a number of reactions illustrated by what has been already given. First, sulphur, or a compound of iron and sulphur, known as iron pyrites, is burned in furnaces to form SO_2 by the aid of oxygen from the air. Then the gaseous sulphurous oxide, fumes of nitric acid and steam are led together into a large lead-lined chamber in which they react on each other as illustrated by the following equations which represent the most recent efforts to explain some rather complex reactions:

$$SO_2 + HNO_3 = \underset{\text{Nitroso-sulphuric acid}}{HO(NO_2)SO_2}$$

This first product, nitroso-sulphuric acid, is decomposed by steam with formation of sulphuric acid and oxides of nitrogen:

$$2HO(NO_2)SO_2 + H_2O = 2H_2SO_4 + NO + NO_2$$

A fresh quantity of sulphurous oxide entering the lead chamber along with air drawn in, and more steam, combine to produce a new quantity of the nitroso-sulphuric acid.

$$2SO_2 + NO + NO_2 + O_2 + H_2O = 2HO(NO_2)SO_2,$$

to be broken up by steam as before, making a continuous process.

The nitroso product may also suffer decomposition in this manner:

$$2HO(NO_2)SO_2 + SO_2 + 2H_2O = 3H_2SO_4 + 2NO$$

The oxide of nitrogen, NO, is easily oxidized and on this the continuity of the process largely depends. It appears, therefore, theoretically, that a very small amount of nitric acid is sufficient to convert an infinitely large amount of sulphurous acid into sulphuric acid. In practice this is not quite true as there is always some loss of the oxidizing gases. Oxygen is supplied by means of a current of air drawn into the chambers, and it is of course necessary to remove the residual nitrogen. In withdrawing this, small amounts of the nitrogen oxides escape and are lost to the process. Several secondary reactions take place which also occasion slight losses. In the following illustration the general arrangement of the lead chambers and furnaces is shown, somewhat diagrammatically.

Sulphur or pyrite is burned in stoves at A, and the fumes with excess of air pass up into the bottom of the tower E. In the upper part of the sulphur burner a little nitric acid is generated by the action of a small amount of sulphuric acid on sodium nitrate and this nitric acid, in vapor, passes along with the air and sulphurous oxide. Steam is generated in the boiler, B, and this is shown as entering the lead chambers at different points. As the several substances come together in the first lead chamber the reactions given above begin but they are not completed until three or four are passed. In the third or largest chamber the principal part of the combination is completed. By the time the last chamber is reached the sulphurous oxide is all in combina-

tion, but mixed with the nitrogen and oxygen from the air there is always some of the oxides of nitrogen. To save these the whole gaseous residue is drawn by means of a tall chimney or blower down into the bottom of the tower C, filled with coke or hard brick; a stream of strong sulphuric acid trickles down over this coke and absorbs the oxides, but allows the other gases to escape. This strong acid with its oxidizing absorbed product flows finally into a reservoir, D, from which it is pumped to a tank above the

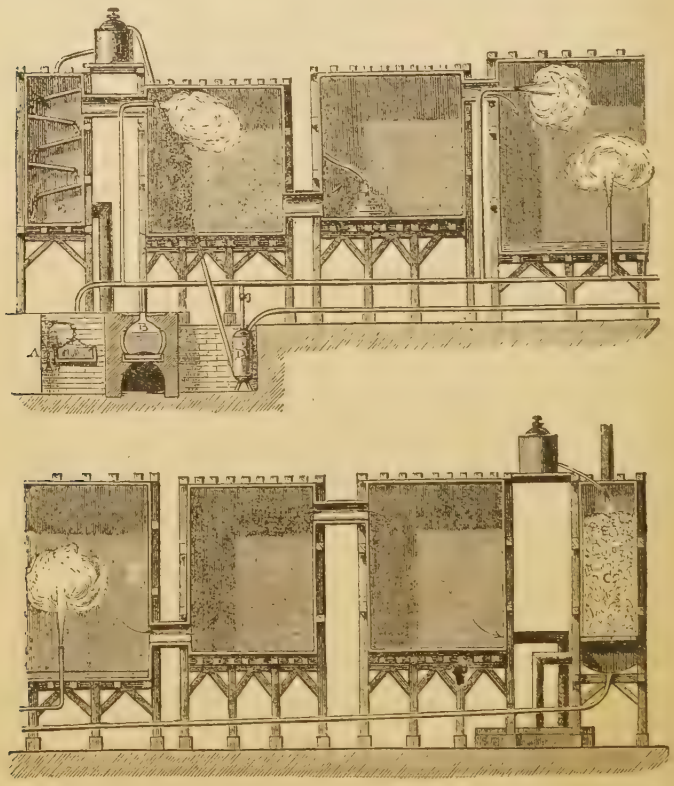


FIG. 18.

first compartment, E, into which it is discharged slowly. Here it meets a stream of water. The dilution causes it to give up the dissolved oxides of nitrogen, because they are not soluble in

weak sulphuric acid. The liberated oxides pass into the first lead chamber again with the sulphurous oxide from the burners and thus remain in circulation. To hasten oxidation a little fresh nitric acid is sometimes allowed to enter the second chamber and flow over the cascade there illustrated. The coke tower to absorb the oxides of nitrogen is called a Gay Lussac tower, and the tower above the burners where the strong mixture is discharged is known as a Glover tower.

The acid formed in the chambers has a specific gravity of about 1.6 and contains about 70 per cent of actual H_2SO_4. This is called chamber acid and is sold for many purposes. A more concentrated acid is produced by boiling down this chamber acid in leaden pans until a product of 1.70 to 1.72 specific gravity is reached; this contains 77 to 80 per cent of acid and is strong enough for most chemical decompositions. Concentration cannot be carried beyond this in lead because it dissolves in strong acid. The most concentrated acid of commerce is made by evaporation in large glass globes or in platinum pans. The purest acid is distilled from platinum stills, which increases its cost considerably.

It was explained above that sulphur trioxide may be made by passing a mixture of oxygen and sulphur dioxide over finely divided platinum. The problem of carrying this reaction out on the large scale was successfully solved some years ago and now in certain factories enormous quantities of "contact" acid are made. The process consists in passing air and purified pyrite burner gas over the contact mass at some definite temperature. The SO_3 produced is combined with water to form an acid of any desired strength. This process will probably displace the other in time.

Properties. Pure sulphuric acid has a specific gravity of 1.838 at 15°. It is colorless and oily in appearance. When heated it decomposes slightly, and if the temperature of ebullition, about 338°, is reached an acid of 98.5 per cent strength is left. This acid may be distilled without further change. Acids of from 94.5 per cent to 99.5 per cent strength have a greater specific gravity than the 100 per cent acid. Commercial sulphuric acid contains

several impurities and is often brownish in color from the presence of traces of organic matter. It is seldom stronger than 95 per cent, and is often below 90 per cent. The specific gravity of this acid is usually between 1.81 and 1.83 at 15°. Large quantities of weaker acids are made and sold for special purposes. The so-called *chamber acid* is sold without concentration, just as it leaves the lead chambers, and is used in several industries.

Strong sulphuric acid has a remarkable action on water, which is shown in the next experiment:

Experiment 115. Pour about 5 Cc. of water into a beaker or test-tube and add to it, stirring meanwhile, about double its volume of strong sulphuric acid. *Pour the acid into the water, not the reverse.* It will be noticed that the mixture becomes very hot, and that steam even may escape. This is a very characteristic behavior of the acid.

Experiment 116. Pour 10 Cc., about, of strong sulphuric acid into a small beaker, which leave uncovered but protected from dust for several days. Notice at the start the depth to which the acid fills the beaker. From time to time look at it and observe that the liquid layer gradually grows deeper. If the beaker can be allowed to stand some weeks a very marked increase in the volume of the liquid will be seen. At the end of this long period repeat the last experiment by pouring the acid into water. A very high temperature on mixing will not be observed now. In fact, if the acid can be allowed to stand long enough, an increase in temperature may be scarcely perceptible.

Another curious reaction depending on the same affinity of sulphuric acid for water is shown in the next experiment. In this case a compound is decomposed and the elements of water, hydrogen and oxygen, abstracted.

Experiment 117. Make a very strong solution of cane sugar by dissolving about 20 Gm. in half its weight of water, in a beaker holding 300 Cc. or more. Pour into the syrup thus made an equal volume of strong sulphuric acid. In a few seconds the mixture becomes hot, blackens and gives off steam. A large volume of loose, finely divided carbon separates and rises to fill the beaker, carried up by the hot vapor. The sugar is a combination of carbon with hydrogen and oxygen; the last two are taken by the acid in the form of water, while the carbon is left in the free state. Ordinary pine wood has a composition very similar to that of sugar. When a splinter is dipped in strong sulphuric acid it blackens for the same reason.

The best tests we have for the recognition of sulphuric acid in the free state depend on the principles just illustrated. Sulphuric acid in combination, that is, in sulphates, may be recognized by other tests, illustrated below.

The behavior of strong sulphuric acid when mixed with salt, saltpeter and many other substances is also characteristic. It has been shown that in the case of salt a reaction follows in which hydrochloric acid and sodium sulphate are formed. With saltpeter we obtain nitric acid and potassium sulphate, as shown. It can readily be proven that by heating a substance known as sodium acetate with strong sulphuric acid we obtain acetic acid and sodium sulphate. In general, it may be said, the members of a large and important class of bodies, known as salts, are decomposed by this acid, yielding sulphates and other acids. From chlorides we obtain hydrochloric acid; from nitrates, nitric acid; from acetates, acetic acid; from phosphates, phosphoric acid, and so on. More will be said about these salts later. We speak of sulphuric acid as a *strong* acid, because it is able to produce these decompositions.

The behavior of sulphuric acid with metals is interesting and has been illustrated by several experiments already. Iron and zinc, and many of the less common metals, are dissolved in sulphuric acid, especially when it is diluted, with formation of sulphates and liberation of hydrogen. Copper, mercury and some other metals are dissolved by sulphuric acid when it is concentrated and hot with formation of sulphates and liberation of sulphurous oxide instead of hydrogen, as shown in the case of copper. But at the ordinary temperature the strongest acid has no perceptible action on certain metals. In fact, commercial sulphuric acid is usually shipped in iron drums or "tank" cars.

Uses of Sulphuric Acid. As has been shown, the manufacture of most of the other common acids depends on the use of sulphuric acid. It is also largely used in the decomposition of common salt as a step in the manu-

facture of sodium carbonate by the Leblanc process. It is used in the decomposition of phosphate rocks in the manufacture of phosphatic fertilizers, which is a very important industry. In the manufacture of many organic dye-stuffs the use of strong sulphuric acid is necessary, and, in fact, it is used in some stage in hundreds of technical processes. The refining of petroleum, the production of glucose, the recovery of ammonia from gas liquor and the manufacture of most modern high explosives, are all industries in which this acid is practically necessary. It has become a commonplace remark that the industrial development of a country may well be measured by the amount of sulphuric acid it uses.

Oil of Vitriol or Pyrosulphuric Acid. It was said at the outset that sulphuric acid was first made by distillation of green vitriol. If this substance, which has the formula $FeSO_4.7H_2O$, is dried it loses most of its water and leaves a basic sulphate having the composition $Fe_2S_2O_9$. When this residue is distilled it breaks up as here represented:

$$Fe_2S_2O_9 = Fe_2O_3 + 2SO_3$$

This SO_3 combines with the small amount of water left in the product and produces an acid of the composition $H_2S_2O_7$. This is the real oil of vitriol, pyrosulphuric acid, or fuming sulphuric acid. It was made practically by distilling the dried vitriol in small well glazed earthen retorts. When exposed to the air it gives off SO_3, which combines with moisture to produce white fumes, H_2SO_4 resulting. This very strong acid is made in large quantities for use in the manufacture of organic products known as *sulphonic acids*. Some of these acids are bodies of great practical importance and certain ones among them cannot be made from the weaker acids. The name Nordhausen acid was formerly applied to this strong acid from the place in Germany where most of it was at one time made. But the same strong acid is now made by the SO_3 process, referred to above, and the old process of vitriol distillation has only historical interest.

The Sulphates. Sulphates are salts formed from sulphuric acid by the replacement of its hydrogen by metals. Several illustrations of this have been given. They may be made, also, by combining sulphuric acid with many salts, as explained above. Many of these sulphates are important bodies and most of them are soluble in water. A few are not soluble, and on this fact a method for the recognition of the whole group is based.

Experiment 118. Pour a weak solution of sodium sulphate into each of three test-tubes. To one add some solution of barium chloride, to the second some solution of strontium chloride, and to the third some solution of lead acetate. In each case a white precipitate forms which, after a time, settles to the bottom of the test-tube; without waiting for this, however, add to each one of three tubes some hydrochloric acid and shake the mixture. No change is observed, then warm it, and still no change appears in the first two. A partial solution may result with the third. We have here, therefore, precipitates which are insoluble in water and hydrochloric acid and which contain barium, lead and strontium as sulphates. Of these the barium sulphate is the most characteristic and important. Barium chloride used as above is a test for sulphates, and in works on analytical chemistry it is shown that when properly employed it gives us accurate information concerning the presence of sulphates in complex mixtures even.

The reactions illustrating these precipitations may be given here. First, with barium chloride and sodium sulphate we have:

$$\underset{\text{Barium chloride}}{BaCl_2} + \underset{\text{Sodium sulphate}}{Na_2SO_4} = \underset{\text{Barium sulphate}}{BaSO_4} + 2\underset{\text{Sodium chloride}}{NaCl}$$

Then with strontium chloride we have:

$$\underset{\text{Strontium chloride}}{SrCl_2} + \underset{\text{Sodium sulphate}}{Na_2SO_4} = \underset{\text{Strontium sulphate}}{SrSO_4} + 2\underset{\text{Sodium chloride}}{NaCl}$$

With lead acetate we have:

$$\underset{\text{Lead acetate}}{Pb(C_2H_3O_2)_2} + \underset{\text{Sodium sulphate}}{Na_2SO_4} = \underset{\text{Lead sulphate}}{PbSO_4} + 2\underset{\text{Sodium acetate}}{NaC_2H_3O_2}$$

Barium chloride solution with sulphuric acid itself gives the same white precipitate, but in this case hydrochloric acid is formed:

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$$

It is customary to speak of *free* and *combined* sulphuric acid. The second expression, referring to the sulphates, is not strictly accurate as the whole of the acid is not in combination. But the characteristic part is and hence the use of the term. The same applies to other salts, as the nitrates, the chlorides, and others. All acids have hydrogen in common, but with the hydrogen we have something characteristic for each acid. This characteristic element or group enters as *combined* sulphuric, nitric, hydrochloric or other acid, into the corresponding salts.

Sulphuric acid was referred to above as a *strong* acid. In its behavior with salts of other acids its strength depends largely on the fact that it boils only at a high temperature. But measured by other standards sulphuric acid is not as strong as hydrochloric or nitric acid. In solution in water its degree of dissociation is much less, and therefore in the many reactions which are due to the presence of free hydrogen ions sulphuric acid is not as active as are the two others mentioned. In reactions like the following,

$$H_2SO_4 + 2NaCl \rightleftarrows Na_2SO_4 + 2HCl,$$

carried out in dilute solution the avidity of the hydrochloric acid for the base is found to exceed that of the sulphuric acid. But in the anhydrous condition the hydrochloric acid is dispelled at a relatively low temperature, and finally sulphate only remains. This follows because the one acid is very volatile and the other not. In solution, however, the above reaction is strictly a reversible one.

Sulphuric acid yields two classes of salts, called normal and acid salts. In solution it dissociates in this way, in two stages:

$$H_2SO_4 \rightarrow \bar{H} + H\bar{S}O_4,$$

and the HSO_4 finally, in dilute solution:

$$HSO_4 \rightarrow \dot{H} + S\dot{O}_4$$

These phenomena will be referred to later in discussing the salts.

Other Sulphuric Acids.

Besides the above several other acids containing hydrogen, oxygen and sulphur are known, free or in combination. The most important one of these is called thiosulphuric acid. This exists in the well-known salt, sodium thiosulphate, $Na_2S_2O_3 + 5H_2O$, formerly called *hyposulphite of soda.* This salt is largely used by photographers. The free acid is not stable. Solutions of thiosulphates decompose with liberation of sulphurous oxide and precipitation of sulphur, when mixed with dilute acids.

The names and formulas of other acids are these:

Dithionic acid	$H_2S_2O_6$.
Trithionic acid	$H_2S_3O_6$.
Tetrathionic acid	$H_2S_4O_6$.
Pentathionic acid	$H_2S_5O_6$.

These acids are rare and have no practical importance in the arts. A detailed description of them is not called for in an elementary book.

Of somewhat greater importance are the persulphates and persulphuric acid, discovered not many years ago. The acid has the formula HSO_4, or $H_2S_2O_8$, and is made by the electrolysis of strong H_2SO_4 at a low temperature. This persulphuric acid is not stable, but decomposes with water yielding hydrogen peroxide:

$$H_2S_2O_8 + 2H_2O = 2H_2SO_4 + H_2O_2.$$

It is therefore a strong oxidizing agent. Some of the persulphates are of technical importance. The potassium salt, KSO_4 or $K_2S_2O_8$, is made by electrolysis of potassium acid sulphate, $KHSO_4$ at a low temperature. When warmed with water it decomposes in this way:

$$K_2S_2O_8 + 2H_2O = 2KHSO_4 + H_2O_2.$$

It is employed as an oxidizer. An oxide corresponding has the formula S_2O_7, but is not technically useful in the pure state. It is not stable.

SULPHUR AND HYDROGEN.

Two combinations of these elements are known, but only one of them is important. This is the compound known as hydrogen sulphide.

Hydrogen Sulphide, or sulphuretted hydrogen, occurs in the free state in some volcanic gases and certain mineral spring waters to which it imparts a marked odor. It is produced by the decomposition of vegetable matters containing sulphur, or from animal albuminoids. It can be formed by the direct union of its two elements, hydrogen and sulphur, at a high temperature, but is most easily made by a method quite analogous to that by which hydrochloric acid is made from a chloride, that is by the decomposition of a sulphide by means of some strong acid. We use for this purpose an artificial substance known as the sulphide of iron, or ferrous sulphide, the preparation of which was illustrated in the experiment wherein iron and sulphur were melted together and strongly heated.

When an acid is poured over the ferrous sulphide it is decomposed with production of the hydrogen sulphide, as illustrated by the following equation:

$$\underset{\text{Ferrous sulphide}}{FeS} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Hydrogen sulphide}}{H_2S} + \underset{\text{Ferrous sulphate.}}{FeSO_4}$$

This method of making the hydrogen sulphide is shown in the following experiment:

Experiment 119. Fit a bottle with a funnel-tube and delivery tube as shown in the figure below. Put in it about 20 to 25 Gm. of ferrous sulphide in small lumps and pour through the funnel-tube enough dilute sulphuric or hydrochloric acid to cover the sulphide and the end of the tube. The delivery tube leads down into a dry bottle covered as well as possible during the experiment with a glass plate. The gas is slightly heavier than air and can therefore be collected in this manner, but not perfectly.

After adding the acid, a few minutes must be allowed for the expulsion of air by the liberated gas; then collect several bottles of the latter for experiment. With one bottle show the combustibility of the gas by burning it, as with hydrogen; observe the odor and test the reaction of the product of the combustion

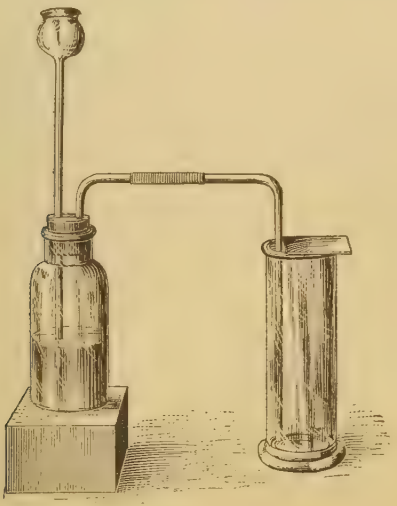


FIG. 19.

by means of litmus paper. With a second bottle of the gas show its solubility in water. To this end cover the bottle with a glass plate, invert it with the mouth under water and then remove the plate. After a time water ascends into the bottle as the gas is absorbed. All this work must be done in a fume closet. The gas is somewhat poisonous.

Experiment 120. After showing the properties of the gas, as above, replace the dry bottles by one containing water. As the gas has been found to be to some degree soluble, a solution known as hydrogen sulphide water is thus obtained. While this solution is being made, prepare weak aqueous solutions of copper sulphate, lead acetate, and zinc acetate and pour them into small flasks or beakers. Twenty-five Cc. of each solution will be sufficient. Remove the bottle containing the water from the generator and in its place put the flask or beaker with the copper sulphate. As the gas bubbles enter this solution a black precipitate forms. In time this precipitate will settle to the bottom of the vessel.

Now take off the delivery tube, wash and replace it and let the gas pass next into the solution of lead acetate. A black precipitate forms here also. Next, after washing the tube, pass the gas into the zinc solution. A precipitate appears here, but it is white instead of black. After a few minutes add to the precipitating mixture half a dozen drops of hydrochloric acid and notice that the precipitate disappears or is dissolved by the acid. Then from a test-tube add ammonia water, a drop at a time, and observe that when a certain amount has been added the precipitate forms again. To the flasks containing the precipitates from the lead and copper solutions add a little hydrochloric acid and notice that the precipitates fail to disappear, as in the case of that from the zinc solution. After these tests have been made, allow the remainder of the gas to bubble into some ammonia water contained in a small flask. This yields a solution of ammonium sulphide, $(NH_4)_2S$. Make all these experiments in the fume closet.

Properties. In the foregoing, some of the most characteristic properties of the hydrogen sulphide have been shown. It dissolves in water just as hydrochloric acid does, but to a much less extent. Most of the gas can be easily expelled by boiling. One volume of water dissolves about two volumes of the gas at the ordinary temperature. Under pressure the gas can be condensed to a liquid which boils at $-62°$.

In the combustion of the gas we have a phenomenon reminding of the behavior of hydrogen, but the flame is weaker and the odor of the product of combustion characteristic. Sulphurous oxide is formed in this experiment, as is illustrated by the equation:

$$H_2S + 3O = H_2O + SO_2.$$

In the moist condition this gas gave the acid test with litmus paper.

The most important behavior of the gas is shown, however, by the precipitation of the three solutions. These precipitates are called *sulphides* and are formed by a double decomposition between the hydrogen sulphide and the substances in solution. The following equations illustrate their production:

$$\underset{\text{Copper sulphate}}{CuSO_4} + \underset{\text{Hydrogen sulphide}}{H_2S} = \underset{\text{Copper sulphide.}}{CuS} + \underset{\text{Sulphuric acid}}{H_2SO_4}$$

$$\underset{\text{Lead acetate}}{Pb(C_2H_3O_2)_2} + H_2S = PbS + 2HC_2H_3O_2$$
(Hydrogen sulphide; Lead sulphide; Acetic acid)

$$\underset{\text{Zinc acetate}}{Zn(C_2H_3O_2)_2} + H_2S = ZnS + 2HC_2H_3O_2$$
(Hydrogen sulphide; Zinc sulphide; Acetic acid.)

As experiment shows and as the equations illustrate, the solutions, though they may be neutral to begin with, must become acid during the precipitation, because acids are formed. The precipitates are therefore insoluble in these acids. That the sulphides of copper and lead are insoluble in hydrochloric acid also was shown above, but zinc sulphide was found to be soluble in hydrochloric acid. This behavior is very suggestive; we are able by it to distinguish between lead and zinc solutions, although both may be colorless. In the one case we get a black sulphide, *insoluble* in hydrochloric acid, while in the other we obtain a white precipitate *soluble* in hydrochloric acid.

To more fully illustrate this important matter let the student carry out the following tests:

Experiment 121. Prepare dilute solutions of mercuric chloride, antimony chloride, ferrous sulphate, zinc sulphate, calcium chloride and sodium chloride. Acidify each one with hydrochloric acid and pass in hydrogen sulphide gas from a generator as before. With the mercury and antimony solutions we obtain precipitates, in the first case black and in the other orange. But in the other cases no precipitates form, even after passing the gas a long time. While the gas is passing add to each solution in turn some ammonia water, and note the result. With the first there is apparently no change, but with the second there is. The orange yellow precipitate dissolves to form a dark yellow solution. In the iron solution we have a black precipitate and in the zinc a white, while in the other solutions no precipitate appears. Add now to these last some solution of ammonium carbonate. In the calcium solution a white precipitate is formed while the other remains clear.

It appears from the above that the mercury compound yields a precipitate in the presence of both acid and alkali, the antimony compound gives a precipitate from the acid solution only, the iron and zinc compounds from the alkaline solution only, while the calcium and sodium com-

pounds give no sulphide precipitates. The iron precipitate is distinguished from the zinc precipitate by its color, while finally the calcium and sodium compounds which give no precipitates with the gas are distinguished from each other by the fact that one yields a precipitate with ammonium carbonate, while the other does not. It should be added here that zinc may be precipitated in presence of *acetic* acid, as well as from alkaline solutions.

These experiments are of fundamental importance, and the student will learn later that they are of common application in the branch of chemistry known as qualitative analysis. The hydrogen sulphide is one of our most important test substances and by its aid we are able not only to recognize bodies in solutions, but to make separations of bodies into groups, and thus isolate them from each other.

We have remaining our solutions of hydrogen sulphide in water and in ammonia water. With these, experiments may be made to show that they behave in many cases as does the gas. Let the student determine for himself their action with solutions. Both are important reagents in the laboratory.

SULPHUR AND CHLORINE.

Three combinations of sulphur with chlorine are known.

Sulphur Monochloride, S_2Cl_2. This is a yellowish brown liquid easily made by passing dry chlorine over sulphur melted in a retort. The liquid has a specific gravity of 1.705 and boils at 138°. It dissolves sulphur readily and in large quantity. The solution so made is used in vulcanizing rubber.

Sulphur Dichloride, SCl_2, is made by passing dry chlorine into the monochloride at a temperature kept near the zero point. It is a dark liquid which decomposes if heated to about 20° or above, yielding free chlorine and the monochloride.

Sulphur Tetrachloride, SCl_4, is made by saturating

the dichloride with chlorine at a temperature of $-22°$. It is a light yellow liquid which decomposes quickly at temperatures above $-22°$.

Sulphur forms also compounds with iodine and bromine, but they are not important.

SELENIUM.

This is a comparatively rare element which resembles sulphur in many respects. It is a solid substance with a dark gray color and melts at about 217°.

The compounds of selenium resemble those of sulphur. The best known are: *selenium dioxide,* SeO_2, a white crystalline substance which dissolves in water to form *selenous acid,* H_2SeO_3; *selenic acid,* H_2SeO_4, made by oxidation of a selenite; *hydrogen selenide,* H_2Se, a gas resembling H_2S and made by decomposing a selenide by an acid, and which precipitates many metals as does the sulphide.

Selenium burns with a disagreeable odor described as resembling that of rotten cabbage, forming an oxide of unknown composition.

TELLURIUM.

Tellurium is another rare element of the sulphur group, found usually in combination as a tellúride. In appearance it resembles the metals, but behaves chemically as do sulphur and selenium. Its specific gravity is 6.2 and its melting point is about 500°. Its most important compounds are: *hydrogen telluride,* H_2Te, a gas; *tellurium dioxide,* TeO_2, a white solid which forms *tellurous acid,* H_2TeO_3, with water; *telluric acid,* H_2TeO_4, a white solid, soluble in water.

The three elements just considered constitute an interesting natural group in which the properties of the elements themselves and of their compounds are functions of the corresponding atomic weights. This is shown in the following table:

	Sulphur.	Selenium.	Tellurium.
Atomic weight	32.1	79.2	127.6
Specific gravity	2.05	4.6	6.2
Melting point	115°	217°	500°
Boiling point	448°	665°	Above 1,000°
Hydrogen compound.	H_2S, gas.	H_2Se, gas.	H_2Te, gas.
—ous oxide	SO_2, a gas, becomes liquid at —8°, soluble in water.	SeO_2, a solid readily soluble in water.	TeO_2, a crystalline solid, slightly soluble in water.
—ous acid	H_2SO_3, not stable in free state.	H_2SeO_3 a solid.	H_2TeO_3, a solid.
—ic oxide	SO_3, volatile solid.	Not known.	TeO_3, yellow crystalline solid.
—ic acid	H_2SO_4, liquid volatile acid not decomposed by HCl.	H_2SeO_4, heavy colorless liquid decomposed by HCl.	H_2TeO_4, white solid mass, with water $H_2TeO_4 + 2H_2O$, crystalline solid.

It will be noticed that the specific gravities, the melting points and the boiling points of the elements increase with the atomic weights. Also that the compounds become heavier or more nearly solids in the same order. It will be pointed out later that similar relations exist between the members of other groups and that in a general way the properties of elements are closely dependent on their atomic weights.

CHAPTER IX.

SILICON AND BORON AND THEIR COMPOUNDS.

These elements occur in nature combined with oxygen or with oxygen and metals.

SILICON.

This is one of the very abundant elements in combination and is found as the oxide, SiO_2, in several minerals of which the most common is quartz. Other substances, flint, white sand, opal, chalcedony and agate, consist essentially of this oxide. In many silicates the element is widely distributed, and it follows oxygen in point of abundance in the earth's crust.

Preparation. The element may be separated by decomposing one of its compounds by potassium, by aid of heat:

$$K_2SiF_6 + 4K = 6KF + Si$$

It is left after this reaction as an amorphous powder. If this is melted with zinc it becomes crystalline as the zinc cools and may be secured in this form by dissolving the metal. Its specific gravity is 2.35 and it is hard enough to scratch glass. As the methods followed in the isolation of silicon are expensive the free element has no technical uses.

SILICON AND OXYGEN.

But one oxide of silicon is known and this has the composition SiO_2, and is called *silica*. It occurs in very pure form in varieties of quartz and tridymite, both characteristic crystalline minerals. In the opal it is found in amorphous condition.

Preparation. Pure silica may be easily made by decomposing a solution of sodium silicate, known as soluble glass, by means of hydrochloric acid. The precipitate which forms is thoroughly washed with water, dried and ignited. This leaves the silica in a fine amorphous condition.

Properties. Silica is practically insoluble in cold water and common acids. It is dissolved, however, by hydrofluoric acid, on which fact the etching of glass depends. At a very high temperature, water (superheated) dissolves silica to a slight extent, forming silicic acid. In alkali solutions, especially if warm, amorphous silica dissolves readily to form silicates. The crystalline varieties of silica may be converted into the same silicates by fusion with alkalies.

SILICIC ACIDS.

Silicon has a valence of four and the acid corresponding to it with the greatest molecular weight has the formula H_4O_4Si, and is known as orthosilicic acid. Its composition is represented in this manner:

$$\left.\begin{matrix} H-O\diagdown \\ H-O- \\ H-O- \\ H-O\diagup \end{matrix}\right\} Si$$

This acid exists in solution, but as it is not stable, cannot be obtained in the free state. An acid derived from this is known:

$$H_4SiO_4 - H_2O = H_2SiO_3,$$

$$\left.\begin{matrix} H-O\diagdown \\ H-O\diagup \end{matrix}\right\} SiO$$

To prepare solutions of these acids a *weak* solution of water-glass is decomposed by hydrochloric acid, leaving orthosilicic acid dissolved. The mixture is thrown on a dialyzer, floating on water, and allowed to remain until it

is free from hydrochloric acid and chlorides. These substances pass through the membrane bottom of the dialyzer, but the colloidal silicic acid cannot. In this manner it is possible to prepare a weak, pure solution of the ortho acid. This may be concentrated to a strength of about 14 per cent.

When evaporated beyond this, water is lost and the gelatinous acid, H_2SiO_3, is formed. This in turn by loss of water becomes SiO_2.

$$H_2SiO_3 - H_2O = SiO_2$$

Silicates.

Corresponding to the silicic acids a large number of bodies called silicates are known. Some of these can be formed artificially, but most of them occur in nature as mineral species, many of which are common and important bodies. The composition of most of these minerals appears quite complex, but a little study shows their relation to orthosilicic acid. For instance, the mineral *serpentine* may be represented by the formula $Mg_3Si_2O_7$, which corresponds to an acid, $H_6Si_2O_7$. Now, this in turn is related to the ortho acid, as illustrated:

$$2H_4SiO_4 = H_6Si_2O_7 + H_2O$$

The common mineral *orthoclase* is called a trisilicate, and is represented essentially by the formula $AlKSi_3O_8$, corresponding to $H_4Si_3O_8$.

This is

$$3H_4SiO_4 - 4H_2O = H_4Si_3O_8$$

It appears, therefore, that these silicates may be looked upon as derived from condensed silicic acids, formed from orthosilicic acid by loss of water. It will be pointed out that boric acid behaves much in the same way.

The silicates of the alkali metals are soluble in water. These solutions have an alkaline reaction because of strong hydrolysis. Potassium silicate and sodium silicate are called soluble glass or water-glass.

Experiment 122. Take about 5 Cc. of the strong solution of sodium silicate, known as water-glass, and add to it, a little at a time, some concentrated hydrochloric acid. When the mixture becomes quite strongly acid a gelatinous mass is produced, which becomes so stiff that the test-tube in which it is formed may be inverted without spilling it. The thick, colloidal substance is impure orthosilicic acid and metasilicic acid.

If, before adding the hydrochloric acid, the water-glass is largely diluted with water no separation of the colloidal substance takes place. It remains in solution and can be partially purified by dialysis, as explained above.

Silicic acid forms insoluble salts with many basic bodies, and some of these can be made by precipitation, as shown below:

Experiment 123. Dilute the common water-glass with about 20 parts of water. Take small portions of this diluted liquid in test-tubes and add to them solutions of calcium chloride, copper sulphate, lead nitrate and cobalt nitrate. Precipitates are formed which are silicates of the metals in these salts.

The soluble glass has approximately the composition Na_2SiO_3 and the insoluble silicates may be made from it by double decomposition, as:

$$\underset{\text{Sodium silicate}}{Na_2SiO_3} + \underset{\text{Calcium chloride}}{CaCl_2} = \underset{\text{Calcium silicate}}{CaSiO_3} + \underset{\text{Sodium chloride}}{2NaCl}$$

A soluble salt is left in the liquid. Advantage is taken of this behavior of the soluble silicate, or water-glass, in making certain kinds of cement and artificial stone.

As mentioned, the alkali silicates are soluble; the others are insoluble in water and many of them cannot be decomposed by acids. Common glass is an artificial mixture of silicates made by fusing quartz sand, silica, with basic substances. For example, common window glass is made by fusing a mixture, in certain proportions, of sand, lime or pure limestone and dry sodium carbonate.

Roughly speaking, we distinguish four varieties of glass, viz.: crown or window glass, Bohemian glass, flint glass and common bottle glass.

Crown Glass is essentially a mixture of calcium and

sodium silicates. In some kinds a little alumina is present. It is made by melting at a very high heat a mixture of white sand, lime or limestone, and soda ash or dry sodium sulphate. Common window and plate glass and much hollow ware are included under crown glass.

Bohemian Glass consists essentially of the silicates of potassium and calcium. It is made of carefully selected materials, usually quartz sand, pure refined potassium carbonate and chalk, or well burned lime, as free as possible from magnesia. This glass can be fused only at a high temperature, and softens only with difficulty when heated. It is, therefore, employed in making much chemical glassware. Sometimes a little sodium carbonate is used with the potassium carbonate to make it more readily workable.

Flint Glass is essentially a lead-potassium silicate and is made by melting a combination of sand, red lead and dry potassium carbonate. This glass can be melted and cast or otherwise worked with comparative ease, and is therefore employed in making tableware and large articles of ornamentation. The ready fusibility depends on the presence of lead silicate. This glass cannot be used for chemical ware.

Common Green Bottle Glass resembles crown glass, but is made of impure materials. It usually contains considerable quantities of iron and aluminum silicates. The green color is due to the ferrous salt.

The chemical composition of several kinds of glass as found by analysis is given in the following table, the results being expressed in the usual manner. It must be remembered, however, that certain special kinds of glass contain still other substances. A part of the silicic acid may be replaced by boric acid and for some purposes the oxide of lead may be partly replaced by oxide of thallium. The relation of glass to pottery will be shown later.

Coloring Glass. Certain metallic oxides may be melted with the glass mixture and so impart to the finished glass some desired shade. The red oxide of copper

Kind of Glass.	SiO_2	Na_2O	K_2O	CaO	MgO	PbO	Fe_2O_3	Al_2O_3
Bohemian.								
Combustion tubing ...	74.19	1.87	13.13	9.39	0.36			0.49
" " ...	76.41	1.38	10.96	9.77				0.89
Optical glass.....	75.81	2.00	15.03	12.13	0.32			1.02
Mirror plate	75.81	4.84	11.39	7.38	0.10			1.01
Flint Glass.								
German	75.24		12.51	1.48		10.48		
English	51.40		9.40			37.40		2.00
Optical	44.30		11.75			43.05	0.50	0.12
Crown Glass.								
German window	71.56	12.97		13.27			1.29	
English window	70.71	13.25		13.38			1.92	
French plate.....	73.00	11.50		15.50				
English plate	77.90	12.53	1.72	4.85			3.59	
German plate	78.75	13.00		6.50			1.75	

is used in making ruby glass, while the black oxide of the same metal gives a green color; ferrous oxide yields a green glass and ferric oxide a yellowish brown; the black oxide of manganese is used in giving a pink to purple, oxide of cobalt a deep blue, oxide of uranium a beautiful canary yellow. Various shades may be made by properly combining some of these oxides, and it is also possible by the proper combination to secure from impure materials an almost colorless glass. Black oxide of manganese is commonly employed to correct the objectionable color due to presence of iron. This it does by oxidizing the iron to the ferric condition, the yellow tint of which is complementary to the purple of the manganese compound.

SILICON AND HYDROGEN.

One compound of these two substances is known, having the composition SiH_4. It is a gaseous body, made by the action of acids on magnesium silicide and is an interesting compound from a theoretical standpoint, but has no technical applications.

SILICON AND THE HALOGENS.

Silicon exists in combination with fluorine, chlorine, bromine and iodine. Of these the tetrafluoride, SiF_4, is

the most important. The formation of this in the etching of glass has been referred to already. It is produced by the action of hydrofluoric acid on silica:

$$4HF + SiO_2 = SiF_4 + 2H_2O$$

It is a gaseous substance which is decomposed by contact with water.

The compounds $SiHCl_3$ and $SiCl_4$ are known. They are volatile liquids which decompose when mixed with water.

Fluosilicic Acid. When silicon tetrafluoride is passed into water it decomposes in this way:

$$2SiF_4 + 3H_2O = H_2SiF_6 + 2HF + H_2SiO_3$$

The body H_2SiF_6 is known as fluosilicic acid. It is stable only in solution, and in this form is sometimes used as a reagent.

BORON.

This is an element which is found in a few natural substances, of which borax, boric acid and calcium borate are the most important. The element may be liberated by the decomposition of some of its compounds, but it is not important in the free state. The specific gravity of crystallized boron is 2.68.

BORON AND OXYGEN.

One compound is known having the composition B_2O_3. It is a glass like body, soluble in water, made best by strongly heating boric acid.

BORIC ACID.

This is a combination of boron with hydrogen and oxygen, having the composition H_3BO_3. It is found in nature in small amount, and especially in the vapor from volcanic fissures existing in certain parts of Tuscany. The water condensed from this vapor is collected in small lagoons, and kept boiling by the action of the hot vapor

itself. In this way a rapid concentration is effected. Much of the boric acid of commerce comes from this source. It can be made from borax, however, and this will be illustrated here.

Experiment 124. By the aid of heat dissolve about 30 Gm. of powdered borax in about 120 Cc. of water. Add to the hot solution enough strong hydrochloric acid to make the liquid strongly acid to litmus paper. Stir well while adding the acid. Then allow the mixture to cool thoroughly. Thin crystalline plates of boric acid separate. Remove the supernatant liquid by filtration, take up the boric acid with hot water and purify it by recrystallization.

Experiment 125. Boric acid is much more soluble in hot water than in cold. It is also readily soluble in alcohol. Prove this by dissolving the product of the last experiment in some alcohol. Pour some of the solution so obtained over a little asbestos in a porcelain dish. When the asbestos is thoroughly moistened take it up with clean forceps and hold it in the flame of the Bunsen burner to ignite the alcohol. The flame produced is colored an intense green by the vaporized boric acid. This is a characteristic reaction and is employed for the recognition of boron compounds.

Considerable quantities of boric acid and borax are now made from borocalcite, $CaB_4O_7.4H_2O$, which occurs abundantly in California.

Borax. This substance is a salt containing boric acid and sodium. Its chemical composition is shown by the formula $Na_2B_4O_7 + 10H_2O$. The water here represented is known as water of crystallization, and can be separated by heat, leaving what is known as *borax glass* or *anhydrous borax*. The preparation of this can be shown by a simple test.

Experiment 126. Bend the end of a piece of platinum wire so as to form a loop two or three millimeters across. Heat this in the flame of the Bunsen burner and then dip it while hot in some powdered borax. Heat again and repeat the operation until the loop is well covered. Then hold this in the flame several minutes. The mass swells and gives off steam, but finally fuses together and forms a colorless, clear, glass-like globule, filling the loop, and called the *borax bead*. The composition of this is $Na_2B_4O_7$. This bead has a very important application in analytical chemistry which is illustrated in this manner: While it is still warm bring it in contact with a *minute* particle of cobalt oxide

or other compound of this metal. The substance sticks to the hot borax, and when the bead is again fused in the flame dissolves in it completely, imparting a blue color, best seen when the bead cools. Many other metals are dissolved from their combinations by the borax in the same manner, imparting some color which is characteristic of the metal. It will be shown later that nickel gives a yellowish brown color, manganese a pink, copper a bluish green color, and other metals other shades.

The amount of copper, cobalt, nickel, manganese or other body necessary to impart color to the borax bead is very small, and hence the test is a very delicate one for the recognition of traces of these substances. The solution of these different substances in the fused borax depends on the formation of new compounds which are known as *double* borates. The boric acid which enters into the composition of borax is capable of holding or uniting with a much greater proportion of the basic substance than is already present. Hence we have sodium-cobalt borate, sodium-nickel borate and so on.

The explanation of this interesting behavior will appear if we look into the nature of boric acid itself. The structure of boric acid is represented in this way:

$$\begin{matrix} H-O\diagdown \\ H-O-B \\ H-O\diagup \end{matrix}$$

This is called orthoboric acid, as the compound H_4SiO_4 is called orthosilicic acid, and the various borates are formed by replacing the hydrogen by metallic atoms. The orthoborates are represented by the composition M_3O_3B, where M stands for an atom with unit valence.

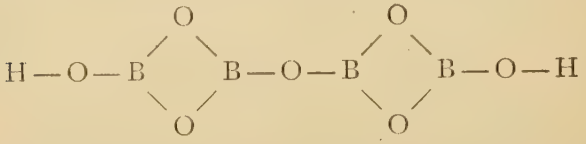
These orthoborates, however, are not common substances, but the so-called metaborates are more stable and more common. Metaboric acid is derived from the ortho acid by loss of water:

$$H_3BO_3 - H_2O = HBO_2$$

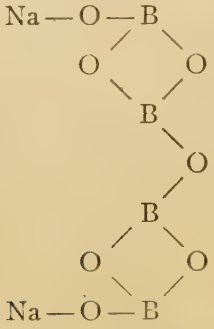
Finally we have another acid still more condensed, known as pyroboric acid, which may be made by heating boric acid to 140° for some hours:

$$4H_3BO_3 = H_2B_4O_7 + 5H_2O$$

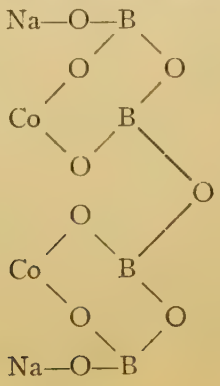
This new acid is a glassy, brittle mass. Its structure may be represented in this way:



The sodium salt, or borax, contains sodium instead of the hydrogen, and we can represent the probable structure as above, or as below, which amounts to the same:



Now, when copper oxide, cobalt oxide or some other metallic compound is fused with borax a union takes place so that bodies of this type, possibly, are formed:



That is, the dissolved metal takes the place of hydrogen in a derived acid. Because of this property of dissolving oxides borax is used by the blacksmith in welding, by the jeweler in soldering and by the assayer as a flux in various metallurgical operations.

Solutions of borax possess an alkaline reaction. This is due to the fact that the salt suffers in part the decomposition known as hydrolysis, as is the case with salts of weak acids in general:

$$Na_2B_4O_7 + 2H_2O = 2NaOH + H_2B_4O_7$$

This complex acid takes up more water and forms the ordinary weak boric acid. The alkalinity of sodium silicate may be explained in the same manner as for borax.

Other Boron Compounds. Boron is found in combination with the halogen elements, in bodies of the type BCl_3. It forms a singular compound with nitrogen, which has the structure BN. It is a white solid decomposed by water in this way:

$$BN + 3H_2O = H_3BO_3 + NH_3$$

Detection of Boron. This element is usually recognized in its compounds by the flame test, as explained above. The compound is mixed with a little sulphuric acid, to liberate boric acid, and alcohol. When the latter is ignited, as explained, the flame shows a green color in presence of boric acid. Boric acid is also recognized by the brown color it imparts to paper moistened with solution of turmeric. This color is not discharged by hydrochloric acid.

CHAPTER X.

PHOSPHORUS AND ARSENIC AND THEIR COMPOUNDS.

PHOSPHORUS.

Occurrence. This element is never found free in nature, but occurs always combined with oxygen and metals. It is most abundant in calcium phosphate, $Ca_3(PO_4)_2$, which is found in bones and in several minerals, and also in amorphous deposits. There are also a number of other minerals which contain phosphorus; it is found in several of the body tissues and is excreted as a phosphate in the urine.

History. Phosphorus was first obtained by Brand, an alchemist of Hamburg, about the middle of the seventeenth century. It was produced from urine in an attempt to discover a process for the conversion of base metals into gold. The general process was somewhat improved by others, but for years the price of the element remained very high. In 1771 Scheele showed how it could be made from bone ash, in which it was discovered a few years before. Phosphorus is now used for several purposes, so that its manufacture has become an important industry.

Preparation. On burning bones a white residue, known as bone ash, and consisting mainly of calcium phosphate, is left. From this the phosphorus of commerce has been usually obtained by the following general method. The bone ash is mixed with crude sulphuric acid, somewhat diluted, which brings about a decomposition illustrated by the following equation:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4$$

The *insoluble* calcium phosphate is converted into a soluble compound containing less calcium, and known as calcium hydrogen phosphate. The solution of this, $CaH_4(PO_4)_2$, is separated from the insoluble calcium sulphate, $CaSO_4$, and is evaporated to dryness and then strongly heated. By this treatment water is driven off and a compound known as calcium metaphosphate is left:

$$CaH_4(PO_4)_2 = Ca(PO_3)_2 + 2H_2O$$

The calcium metaphosphate is then mixed with charcoal and distilled from clay retorts. Free phosphorus passes over in the form of vapor, which is condensed under water to a liquid and afterward run into molds to cool, thus forming the sticks as seen in commerce. The chemical changes occurring in the distillation of the mixture from the clay retorts have been found to take place in a manner illustrated by this equation:

$$3Ca(PO_3)_2 + 10C = P_4 + Ca_3(PO_4)_2 + 10CO$$

The action of the charcoal here is that of a *reducing agent,* to remove oxygen.

At the present time phosphorus is largely produced in the electric furnace by decomposing a mixture of a phosphate and powdered coke or charcoal. The intense heat of the electric arc makes this method of liberating phosphorus a very simple one. From the electric furnace the phosphorus distills and is condensed under water, as in the older process.

Properties of Phosphorus. In perfectly pure condition phosphorus is a *white* wax-like solid. The commercial product is always yellowish. It may be cut readily with a knife. It melts at a temperature of 44.2° C. and has a specific gravity of about 1.83. It boils at about 290°. When heated to a certain temperature in an atmosphere free from oxygen it forms *red phosphorus,* which will be referred to below. Other properties have been illustrated already in the experiments with oxygen, and in the analysis of air. Phosphorus was found to

combine very readily with oxygen. It combines directly with other elements, as illustrated in the next experiments.

Experiment 127. Place a very small piece of dry phosphorus in a porcelain crucible or evaporating dish and add a few small crystals of iodine in such a manner as to bring the two substances into actual contact. Very soon a combination takes place accompanied by light and heat.

Experiment 128. In a dry flask or bottle with a wide neck warm a few drops of bromine until the vapor fills the vessel. Put a small piece of dry phosphorus in a deflagrating spoon and immerse this in the vapor. The phosphorus combines quickly with the bromine.

In the first of these experiments iodide of phosphorus is formed, and in the second bromide of phosphorus. Compounds of chlorine are known, made by direct union.

Solubility of Phosphorus. Common phosphorus is not soluble in water, but is dissolved by several other liquids. One of the best solvents is carbon disulphide, CS_2. The action is shown in the following experiment:

Experiment 129. Pour about 5 cubic centimeters of carbon disulphide into a test-tube, and add a very small piece of phosphorus, *not larger than a small pea.* Cork the tube and set it aside a few minutes, with occasional shaking. The phosphorus soon dissolves. Put a sheet of filter paper on a brick or flat stone, and pour the solution from the test-tube over the paper. *Leave none of it in the tube.* Allow the paper to stand for the spontaneous evaporation of the disulphide. This is complete in a few minutes, and then the phosphorus, spread over the whole paper, bursts into flame, combining suddenly with the oxygen of the air. Before putting the test-tube away heat it to oxidize any trace of phosphorus left in it, to avoid accidents.

Common phosphorus is violently poisonous when taken into the stomach, and many fatal cases are on record. This property is probably due to its great affinity for oxygen, as the oxidized compounds of the element are nonpoisonous.

Uses of Phosphorus. It is largely employed in the manufacture of matches, the heads of which, in some cases, consist of phosphorus and gum arabic. Because

of the danger to workmen in factories where matches are made, the use of common phosphorus has been in many places abolished. The red variety, to be described, is often used instead. Phosphorus is also largely used in the manufacture of several of its important compounds.

Amorphous Phosphorus.

A peculiar modification of phosphorus exists, known as *red* or *amorphous* phosphorus. This substance has few of the marked properties found in the ordinary variety. It is not poisonous and is insoluble in carbon disulphide. When heated to a temperature of about 250° C. the common white phosphorus is changed to the red variety, and the latter at a temperature of about 300° is changed into the white form again. This can be illustrated by an experiment.

Experiment 130. Heat a little red phosphorus in a narrow glass tube sealed at the lower end. At the proper temperature a light colored product is formed, which vaporizes and collects on the cooler part of the tube above the flame. That this is the ordinary phosphorus can be shown by breaking off the sealed end of the tube and heating again. Air now having access, combustion of the phosphorus soon follows.

Red phosphorus may be also made by heating the common variety in closed vessels to a temperature of 10° above its boiling point. The change then is very rapid. This form of phosphorus may be used with perfect safety in the match industry and is largely prepared for that purpose. It has a specific gravity of 2.1 and is as hard as marble. In commerce it appears usually in the powdered form.

The so-called "safety matches" do not usually contain phosphorus. The heads of these are covered with a mixture of oxidizing substances, and ignition is secured by rubbing on a surface impregnated with red phosphorus. The head mixture contains usually potassium chlorate and antimony sulphide.

PHOSPHORUS AND HYDROGEN.

Three compounds of these elements are known, called hydrogen phosphides:

PH_3, a gas.
P_2H_4, a liquid.
P_4H_2, a solid.

The first one is very easily made, and is usually accompanied by a small amount of the second or liquid product. The latter is spontaneously inflammable, and ignites the other on coming in contact with the air. The preparation of the gaseous product is shown in the experiment now to be given:

Experiment 131. Arrange the apparatus as shown in the figure. The flask has a capacity of about 250 to 300 Cc. Two-thirds fill it with a strong solution of potassium hydroxide, and throw in a small piece of phosphorus not larger than a pea. Add

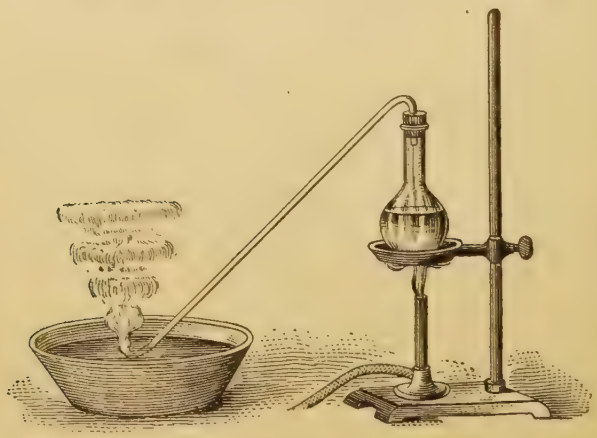


FIG. 20.

a few drops of ether, insert the cork with the bent delivery tube, and apply heat gradually. The ether on evaporating serves to drive the air out from the upper part of the flask. The delivery tube is bent so that its lower end, which is turned upward,

dips beneath the surface of water in the basin. When the liquid becomes warm a combination between the alkali and the phosphorus takes place, by which the gaseous hydrogen phosphide is liberated. This, with a trace of the liquid product, escapes through the delivery tube, and as soon as it bubbles through the water into the air, ignites spontaneously. In the combustion phosphoric oxide is formed, which takes the shape of a ring, expanding as it ascends through the air. Do not remove the lamp or the tube from the water until the reaction is terminated. Then lift the tube from the water first, remove the lamp, and allow the apparatus to cool. The gas is poisonous, therefore the fittings must be tight.

The phosphorus and alkali react on each other in a manner shown by the following equation:

$$P_4 + 3H_2O + 3KOH = \underset{\text{Potassium hypophosphite}}{3KH_2PO_2} + PH_3$$

When the gas burns in the air we have:

$$2PH_3 + 4O_2 = P_2O_5 + 3H_2O$$

The gas PH_3 is commonly called phosphine. It forms several combinations resembling those formed by ammonia, and these are known as phosphonium compounds; phosphonium bromide is formed by the direct combination of the gases PH_3 and HBr,

$$PH_3 + HBr = PH_4Br$$

The spontaneously inflammable gas is made also by decomposing calcium phosphide with water. In the reaction some liquid hydrogen phosphide is formed, and this may be separated by passing the gaseous mixture through tubes immersed in a freezing bath. A colorless liquid condenses and this burns spontaneously on exposure to the air. This liquid, P_2H_4, is not stable but decomposes, yielding P_4H_2, a yellow solid, and PH_3.

PHOSPHORUS AND OXYGEN.

Phosphorus forms four or five oxides, but only two of them are important. They are the trioxide, P_4O_6, and

the pentoxide P_2O_5. Corresponding to these oxides are two acids, phosphorous acid, H_3PO_3, and phosphoric acid, H_3PO_4. A third acid known as hypophosphorous acid has the composition H_3PO_2.

Hypophosphorous Acid. A salt of this acid was produced in the last experiment. In the flask, after the completion of the reaction, we have the solution of a substance known as potassium *hypophosphite*. Other bodies called hypophosphites are made on the large scale by replacing the potassium hydroxide by different alkali substances. Some of these products have technical value and are used in medicine. The free acid is made by decomposing the hypophosphite of barium by the proper amount of dilute sulphuric acid:

$$Ba(H_2PO_2)_2 + H_2SO_4 = BaSO_4 + 2H_3PO_2$$

A concentrated thick, syrupy liquid is obtained by evaporating the filtrate from the barium sulphate.

The acids and the salts are all strong reducing agents, because of the tendency of the phosphorus to combine with more oxygen. A solution of sodium hypophosphite is often used in analytical chemistry for the precipitation of certain metals. In the salts of hypophosphorous acid but one atom of hydrogen of the acid may be replaced; they are all, therefore, of the type H_2NaPO_2, and only one hydroxyl group can be present in the acid.

Phosphorus Trioxide. This is a white powder, made by the incomplete combustion of phosphorus in a stream of air or oxygen diluted with carbon dioxide. It dissolves in water, forming the acid known as phosphorous acid, H_3PO_3:

$$P_4O_6 + 6H_2O = 4H_3PO_3$$

Neither the oxide nor the acid is important. The salts of the acid are known as phosphites. In all of them, as far as known, but two of the hydrogen atoms of the acid are replaced. Phosphorous acid may be made in purest form by decomposing the chloride, PCl_3, with water.

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

Phosphorus Pentoxide. This is the common oxide produced when phosphorus burns in the air or in a sufficient supply of oxygen. It is a soft, white substance, characterized by its powerful affinity for water, in which it dissolves, forming phosphoric acid. It is produced in large quantities for use in the drying of gases, for several chemical reactions in organic chemistry, and also as a step in the manufacture of phosphoric acid from phosphorus.

Phosphoric Acids. When the pentoxide dissolves in cold water this reaction follows:

$$P_2O_5 + H_2O = 2HPO_3$$

The substance produced here is known as metaphosphoric acid. It is not stable permanently in solution; on standing more water is taken up, and the orthophosphoric acid, H_3PO_4, is formed. This change follows very quickly by boiling the solution of the metaphosphoric acid.

Orthophosphoric acid may be made as just described, or it may be produced by the oxidation of phosphorus by means of nitric acid. It is also largely produced from pure bone ash, mainly calcium phosphate, by separation of the bases. The pure acid appears in commerce as a thick, syrupy liquid, which sometimes deposits crystals on standing. This is the common phosphoric acid of the pharmacopœia and is much used in medicine. It mixes with water in all proportions, and is stable at ordinary temperatures. At a temperature a little above 200° the pure ortho acid loses water and yields an acid known as pyrophosphoric acid, $H_4P_2O_7$.

$$2H_3PO_4 - H_2O = H_4P_2O_7$$

Pyrophosphoric acid is a crystalline body easily soluble in water. All of the hydrogen may be replaced to form salts, some of which are quite important. Sodium pyrophosphate, $Na_4P_2O_7$, is most easily made by heating the common phosphate, HNa_2PO_4, to redness. A mole-

cule of water is driven off and the pyrophosphate results. Pyrophosphates yield with silver nitrate a white precipitate, $Ag_4P_2O_7$, while orthophosphates yield a yellow precipitate of Ag_3PO_4. The common pyrophosphates are stable in cold solution; on long boiling they revert to orthophosphates. This change is quickly effected by heating with acids.

Metaphosphoric acid is formed from orthophosphoric acid by evaporating to complete dryness and then igniting strongly. It forms a solid glassy mass and is commonly known as glacial phosphoric acid. It dissolves readily in water, and, as explained, this solution yields the ortho acid on boiling. Solutions of metaphosphoric acid yield white precipitates with egg albumin and with calcium chloride. These precipitates do not form with the ortho and pyro acids.

The three phosphoric acids may be looked upon as related to each other in this manner:

$$P_2O_5 + H_2O = 2HPO_3$$
$$P_2O_5 + 2H_2O = H_4P_2O_7$$
$$P_2O_5 + 3H_2O = 2H_3PO_4$$

Orthophosphoric acid has three replaceable hydrogen atoms, or is tribasic; it forms therefore three classes of salts.

H_3PO_4 is phosphoric acid.
H_2NaPO_4 is dihydrogen sodium phosphate.
HNa_2PO_4 is hydrogen disodium phosphate.
Na_3PO_4 is trisodium phosphate.

The salt $HNa_2PO_4 + 12H_2O$ is known as common sodium phosphate. It is used in the laboratory as a test reagent.

Tests for Phosphoric Acid. Orthophosphoric acid and the orthophosphates are recognized by several tests. They yield a yellow precipitate with silver nitrate, a white crystalline precipitate with an alkaline solution containing ammonia, ammonium chloride and magnesium chlo-

ride, and finally a very characteristic yellow precipitate with a solution of ammonium molybdate. This is a delicate test and will be here illustrated.

Experiment 132. Take a few cubic centimeters of a phosphate solution in a test-tube, add several drops of strong nitric acid and then some solution of ammonium molybdate. Allow the test-tube to stand at rest ten minutes. A fine yellow crystalline precipitate settles out. This precipitate is soluble in ammonia water, as can be seen by trial. The composition of this crystalline substance is complex, but is probably $(NH_4)_3(MoO_3)_{12}PO_4$.

The meta and pyrophosphates in nitric acid solution, after heating, yield exactly the same test.

PHOSPHORUS AND THE HALOGENS.

Phosphorus forms important compounds with chlorine, bromine and iodine by direct union.

Phosphorus Trichloride is a colorless liquid obtained by passing dry chlorine gas over phosphorus heated in a retort. The phosphorus burns in the chlorine atmosphere and the product distills over into a dry, cool receiver. The trichloride boils at 76°. It fumes in the air and is decomposed by water.

$$PCl_3 + 3H_2O = 3HCl + H_3PO_3$$

The reaction just illustrated is one of very great importance in the decomposition of bodies which, like water, contain the hydroxyl group, OH. In organic chemistry the chlorides and bromides of phosphorus find extended applications in the preparation of halogen derivatives of acids and alcohols, which contain the OH group. In illustration, the formula of common alcohol is C_2H_5OH, and this combines with PCl_3 or PBr_3 in this manner:

$$3C_2H_5OH + PCl_3 = 3C_2H_5Cl + H_3O_3P,$$

or, expressed graphically,

$$\begin{matrix} C_2H_5OH \\ C_2H_5OH \\ C_2H_5OH \end{matrix} + P \left\{ \begin{matrix} Cl \\ Cl \\ Cl \end{matrix} \right. = \begin{matrix} C_2H_5Cl \\ C_2H_5Cl \\ C_2H_5Cl \end{matrix} + \left. \begin{matrix} HO \\ HO \\ HO \end{matrix} \right\} P$$

Acetic acid has the composition C_2H_3OOH. This reacts with the trichloride as follows:

$$3C_2H_3OOH + PCl_3 = 3C_2H_3OCl + H_3O_3P,$$

acetyl chloride and phosphorous acid being formed.

The student should note these typical reactions carefully, as he will have occasion to use them in the study of the complex compounds of carbon. The pentachloride of phosphorus, described below, is often used in preference to the trichloride because of its more energetic action.

Phosphorus Pentachloride is made by the continued action of chlorine on the trichloride. The chlorine is absorbed and a dry solid mass results. This is the crude pentachloride which may be purified by sublimation. Like the trichloride it is decomposed by water, forming the oxychloride first:

$$PCl_5 + H_2O = 2HCl + POCl_3$$

An excess of water reacts in this manner:

$$PCl_5 + 4H_2O = 5HCl + H_3PO_4$$

Phosphorus Bromides. Phosphorus and bromine combine directly, forming the tribromide, PBr_3, which is a colorless liquid, boiling at about 175°, and having a specific gravity of 2.925. Phosphorus pentabromide is a yellow crystalline solid, formed by the action of bromine on the tribromide.

Phosphorus Iodides. Two iodides are known, obtained by mixing solutions of iodine and phosphorus in carbon disulphide. After the combination is complete the disulphide may be distilled off, leaving the iodides as crystalline products. By using a certain amount of iodine the iodide P_2I_4 is obtained, while with a larger proportion the tri-iodide, PI_3, is made. The latter resembles the

corresponding chlorine and bromine compounds in its behavior with water:

$$PI_3 + 3H_2O = 3HI + H_3PO_3$$

Advantage is taken of this reaction in the preparation of hydriodic acid.

Two compounds with fluorine, PF_3 and PF_5, are known, as are also several compounds with nitrogen, oxygen and hydrogen. But none of these may be considered important.

ARSENIC.

Occurrence. This element is rather widely distributed in nature, being found in many ores, and also in the free state. The important ores which contain it are realgar, As_2S_2, orpiment, As_2S_3, arsenical pyrite, Fe_2S_2As, arsenical nickel, NiAs, and arsenical iron, $FeAs_2$. Much of the arsenic of commerce is obtained as a by-product in the working of these ores.

History. The sulphides of arsenic have been known from the earliest times and the alchemists were acquainted with the preparation of the white oxide (commonly called arsenic) from these ores. Albertus Magnus, in the twelfth century, first stated that a metal-like substance is contained in this white arsenic, but this view was not commonly admitted until near the end of the eighteenth century when it was experimentally found that the white body is the oxide of arsenic or arsenicum.

Preparation. What is known as metallic arsenic is usually made by the sublimation of arsenical pyrite:

$$Fe_2S_2As = 2FeS + As$$

It may also be obtained by heating the white oxide with powdered coal or charcoal.

Properties. When prepared by reduction, arsenic is a dark steel gray, brittle mass, with metallic luster. It is easily sublimed, yielding a yellow vapor, and at a high

temperature it combines readily with oxygen to form the trioxide. In moist air it oxidizes at the ordinary temperature to form the same oxide. The specific gravity of arsenic is 5.73, and in this and other properties it resembles the true metals. In its combinations, however, it acts usually as a nonmetallic element. It alloys with some of the metals. It hardens lead, and is therefore frequently added to the latter element in the manufacture of shot.

ARSENIC AND HYDROGEN.

Arsenic forms two compounds with hydrogen, one of which, AsH_3, is a gas, while the other, As_2H_2, is a solid. The first only is important. A compound having the formula AsH, probably, has also been described.

Hydrogen Arsenide or Arsine. This gas was prepared by Scheele in pure condition in 1775, and later by Proust. It is always formed when nascent hydrogen is liberated in presence of an arsenic compound in acid solution, and as usually liberated is mixed with a large excess of hydrogen. It may be made in pure condition by the action of sulphuric acid on zinc arsenide:

$$Zn_3As_2 + 3H_2SO_4 = 3ZnSO_4 + 2AsH_3$$

The gas is intensely poisonous and one of the early experimenters, Gehlen, lost his life by inhaling a very small quantity.

It is easily made in impure form by the addition of a solution of any arsenic compound, best neutral or slightly acid, to a hydrogen generator in action. The nascent hydrogen decomposes the compound, as illustrated by this equation:

$$As_2O_3 + 6H_2 = 3H_2O + 2AsH_3$$

The AsH_3 escapes mixed with the excess of hydrogen given off. The student should make the following experiment, *but in a good fume closet or in a good draught of air.*

In no case should more than the minute amount of arsenic compound referred to be taken for experiment.

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Experiment 133. Arrange a hydrogen generator, as already explained and as further illustrated in the figure below. To the generator is attached a drying tube with calcium chloride, and following this is a tube of moderately hard lead-free glass, narrowed slightly in the middle and drawn to a small orifice at the outer end. Charge the bottle with pure zinc, *free from arsenic,* and add pure dilute sulphuric acid in the usual manner. Allow the evolution of gas to continue until the air is all expelled, and then light it at the drawn out end of the delivery tube. The burning gas is pure hydrogen only, if the materials used are pure. In any event, test the gas by holding a clean cold porcelain dish against the flame several minutes. If after five minutes no black stain or deposit appears on the dish the gas may be considered pure for the present purpose. Now prepare a very dilute

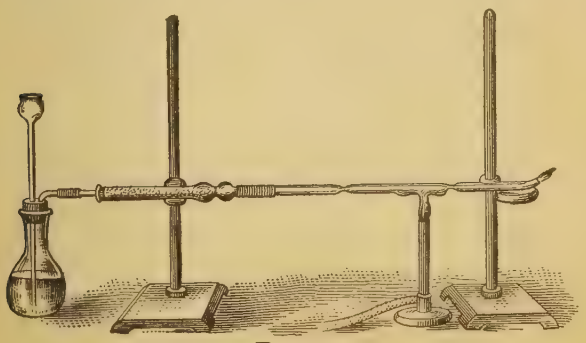

FIG. 21.

solution of sodium arsenite, or arsenous acid, and pour *5 drops* of this through the funnel tube into the generator. Hold the porcelain dish again in the flame and observe that after a time a shining black deposit of arsenic collects. Allow several of these stains or deposits to form on different parts of the dish. (The stains may be further examined as will be explained shortly.) Next heat the delivery tube with the Bunsen flame a short distance in front of the central narrowed part, that is between the generator and the constriction. At a high temperature the hydrogen arsenide decomposes, yielding arsenic, which precipitates on the cooler part of the tube, and hydrogen, which burns at the end. If the heat is applied at the right point the arsenic deposit forms in the contracted portion of the tube where it can be readily seen. The liberated arsenic, being slightly volatile, is deposited some distance beyond the point most strongly heated. The stains in the dish may now be tested. Pour in a few drops of a fresh solution of sodium hypochlorite and allow this to flow

around the dish. The deposit goes into solution almost instantly. This behavior distinguishes arsenic from very similar antimony stains to be described later. *In performing this experiment care must be taken to have the corks and fittings of the apparatus perfectly tight, and to keep the gas burning, after the addition of the arsenic solution.*

The experiment just described constitutes what is called the *Marsh* test for arsenic. It is exceedingly delicate, and further details concerning it may be found in books on qualitative analysis, as it is practically important.

Hydrogen arsenide is not soluble in water to a great extent. One volume of cold water will take up about five volumes of the gas, but the product decomposes on standing. In the above experiment it forms water and arsenous oxide on burning.

$$2AsH_3 + 3O_2 = As_2O_3 + 3H_2O$$

The white oxide imparts a light color to the flame. If the flame is much cooled, as happens when the cold porcelain is held in it, the hydrogen alone burns, forming water, while the arsenic is deposited on the cold surface in the free state, or possibly as solid hydrogen arsenide, AsH.

ARSENIC AND OXYGEN.

Arsenic forms two compounds with oxygen, the trioxide or arsenous oxide, As_2O_3, and the pentoxide, As_2O_5. Both are well known and common.

Arsenous Oxide. This is the body commonly known as white arsenic. It appears in commerce in several forms, as fine powder, granular or massive. The massive, or vitreous, variety is formed by the sublimation of the crude white powder, which is a by-product in the roasting of certain ores containing arsenides. Arsenous oxide has the composition As_2O_3, or As_4O_6 probably. It is slightly soluble in water, the solution containing the hydroxide, $As(OH)_3$, or arsenous acid.

Arsenous oxide is a violent poison, this depending on its solubility in the liquids of the stomach or intestines.

It is easily reduced to the free or metallic condition, as illustrated by the following experiment:

Experiment 134. Cut from a piece of glass tubing having an internal diameter of about 3 to 4 Mm., a length of 20 Cm. Hold this in the flame until it is softened in the middle, then draw it out about 4 Cm. and melt until the two pieces separate, thus making two closed tubes, pointed and sealed at one end. Drop a minute amount of arsenous oxide into one of these tubes and tap until the powder collects in the point. Then drop in a small fragment of charcoal, which is just large enough to fill the wide part of the tube, but which cannot follow the oxide into the extreme point. Now heat the tube in the flame, the part on which the charcoal rests first, and then the pointed end below it. The white oxide is volatilized and passing up comes in contact with the hot charcoal, suffering reduction to the free condition as expressed in this equation:

$$As_2O_3 + 3C = As_2 + 3CO$$

The liberated arsenic collects as a dark mirror on the colder part of the tube above the charcoal. Allow the tube to cool, break off the lower end and heat it again carefully. The current of hot air passing over the arsenic oxidizes it to arsenous oxide, and this forms a white ring higher up if the heat is not too strong.

On the large scale the reduction is effected in iron retorts.

Arsenous oxide, as explained, is but slightly soluble in water. In dilute hydrochloric acid it dissolves, but does not form the chloride. Heated with nitric acid oxidation to arsenic oxide takes place. Alkali solutions dissolve it readily, forming arsenites, as illustrated by this equation:

$$As_2O_3 + 6NaOH = 2Na_3AsO_3 + 3H_2O$$

The subject of the solubility of arsenous oxide in water and other liquids is a very important one from a toxicological standpoint, and much has been written on it. The solubility of the pure oxide has been found to vary much with its physical condition.

The Arsenites. Some of these are common substances. Those of the alkali metals are readily soluble in water and are very poisonous. The arsenites of silver, copper and some other metals are insoluble in water and

appear therefore when a soluble arsenite solution is added to a solution of copper sulphate, silver nitrate, etc. The silver arsenite is yellow; copper arsenite is green. The best known of the arsenites is sodium arsenite, Na_3AsO_3. It is employed for many purposes, especially in the production of the insoluble arsenites and of embalming fluids. Some of the insoluble arsenites have been largely used as pigments, but now, fortunately, they are being displaced by the bright and harmless coal-tar dyes. *Paris green* is a crude product made by precipitating sodium or potassium arsenite by copper acetate. It is essentially copper aceto-arsenite, but of somewhat variable composition. It is known also as *Schweinfurth green, emerald green* and *French green. Scheele's green* is copper arsenite, $CuHAsO_3$. All of these compounds are poisons and should not be used.

The well-known "Fowler's solution" used in medicine contains potassium arsenite.

Arsenic Oxide, As_2O_5. This product is easily made by heating the trioxide with strong nitric acid, which acts as an oxidizing agent.

$$As_2O_3 + 2HNO_3 = As_2O_5 + H_2O + N_2O_3$$

As the oxide is soluble, it is left after the action in the form of arsenic acid, H_3AsO_4. On evaporation and heating to a temperature of about 300° this acid decomposes and leaves the pure anhydrous pentoxide. At a red heat it breaks up into $As_2O_3 + O_2$. The pentoxide is much more soluble in water than the trioxide, and forms a strong solution of arsenic acid.

Arsenic Acid. This acid, as just explained, has the composition H_3AsO_4, and is best made by boiling the trioxide with nitric acid. It appears in commerce as a thick liquid with a strong acid taste, from which a crystalline hydrated solid may be obtained by cooling to a low temperature. At 100° the water of crystallization is lost and the true acid, H_3AsO_4, remains, while at a higher temperature pyroarsenic acid, $H_4As_2O_7$, and finally metarsenic acid, $HAsO_3$, result. These bodies correspond to pyro- and metaphosphoric acids.

Arsenic acid parts with oxygen readily enough to serve as a good oxidizing agent and it is so employed in the manufacture of aniline red on the large scale.

The Arsenates. In its behavior with bases arsenic acid closely resembles phosphoric acid and forms three classes of salts, as Na_3AsO_4, Na_2HAsO_4 and NaH_2AsO_4. The salts of arsenic acid are isomorphous with those of phosphoric acid. With silver nitrate the arsenates yield a *red* precipitate, Ag_3AsO_4, while the arsenites yield a *yellow* precipitate, Ag_3AsO_3.

ARSENIC AND THE HALOGENS.

Compounds of arsenic with chlorine, bromine and iodine are known. The chloride is a heavy liquid best made by passing chlorine gas over heated arsenic; the bromide is a solid, made by adding powdered arsenic to a solution of bromine in carbon disulphide; the iodide is also a solid and is obtained from iodine and arsenic in the same manner. These three compounds decompose with water:

$$2AsCl_3 + 3H_2O = As_2O_3 + 6HCl$$

To decompose the chloride in presence of hydrochloric acid a considerable excess of water is necessary.

ARSENIC AND SULPHUR.

Two sulphides of arsenic occur in nature, realgar, As_2S_2, and orpiment, As_2S_3. They may be both made artificially. Artificial realgar comes into commerce as a ruby red glassy mass, sold as a pigment and as a depilatory for use of tanners. It is made by subliming mixtures of arsenical and common pyrites. Commercial orpiment is known as *King's yellow*, and is made by sublimation of a mixture of sulphur and arsenous oxide. A much purer product is made by precipitating a solution of an arsenite with hydrogen sulphide. A pentasulphide, As_2S_5, is also known as a yellow solid made by fusing

the trisulphide with sulphur. Classes of salts known as sulpharsenites and sulpharsenates exist, corresponding to arsenites and arsenates. K_3AsS_3 and K_3AsS_4 are illustrations.

Antidotes in Arsenical Poisoning. The several antidotes recommended to be given in cases of arsenical poisoning are substances which form insoluble compounds with arsenic acids and salts. Probably the best of these is freshly precipitated ferric hydroxide, which must be well washed with water and administered in relatively large quantity. With arsenous acid or arsenites it forms an insoluble basic arsenite of iron. Magnesia is sometimes used for the same purpose, and a product made by agitation of an excess of magnesia with ferric sulphate solution has also given good results. This contains ferric hydroxide and magnesium sulphate along with magnesium oxide and hydroxide. These antidotes were proposed primarily for arsenous oxide, but they act equally well with most of the other compounds.

Tests for Arsenic.

Because of the great importance of the subject much attention has been given to the tests for arsenic. One of the best of these for the recognition of traces is the Marsh test described above. Another is the Reinsch test, which may be illustrated as follows:

Experiment 135. Pour 10 cubic centimeters of pure diluted hydrochloric acid into a test-tube and add a bit of bright pure copper foil. A piece a centimeter square will answer. Boil the acid a minute or two and observe that the foil remains bright, which must be the case in absence of arsenic. Now add a few drops of a dilute arsenical solution and heat again to boiling. A greyish black deposit forms on the copper and this consists of an alloy of copper and arsenic. This deposit may be obtained from extremely dilute solutions; the test is therefore a very delicate one.

Arsenites and arsenates are often recognized by their behavior with silver solution, and all arsenic compounds yield a precipitate with hydrogen sulphide in properly prepared solutions. The precautions to be taken in applying these tests are explained in books on qualitative analysis

CHAPTER XI.

CARBON AND SOME OF ITS IMPORTANT COMPOUNDS.

We have here a very abundant, and at the same time one of our most important, elements, which is found very widely distributed in nature, in vegetable, animal and mineral substances, and also in the free state. Carbon occurs in the three distinct forms of diamond, graphite and amorphous carbon. Of the last there are several varieties, as charcoal, coke, lampblack and boneblack.

History. Charcoal, graphite and the diamond have been known from remote antiquity, but that they are all varieties of carbon was not recognized until within comparatively recent times. In the seventeenth century it was shown that the diamond may be caused to disappear when placed in the focus of a large double convex lens in bright sunlight. That this disappearance is due to combustion at the expense of the oxygen of the air was shown a hundred years later by Lavoisier and others, who demonstrated that carbon dioxide is produced in the combustion. Scheele showed somewhat earlier that graphite may be converted by oxidation into carbon dioxide, and between 1796 and 1800 it was demonstrated that equal weights of charcoal, graphite and diamond yield the same amount of this gas.

THE DIAMOND.

This variety of carbon is found crystallized in several forms belonging to the regular system. Octahedra are the most common. For hundreds of years attempts have been made to produce the diamond artificially, but always without success until quite recently, when Moissan succeeded in producing very small crystals by subjecting molten cast iron containing carbon to very great pressure.

This pressure was secured by the rapid chilling of the surface of the iron, from which contraction of the chilled layer on the still liquid center followed. The crystals so produced are very small and have no commercial value, but the process is one of great scientific interest and may lead to something more.

Regular and clear forms of the natural diamond are highly prized as gems, while dark and opaque crystals are used, because of their great hardness, in pointing rock drills, and in powder for grinding the gems. The diamond is the hardest substance known. Its specific gravity is 3.5 to 3.6. When heated to a sufficiently high temperature in oxygen the diamond burns to carbon dioxide, leaving only a trace of ash.

GRAPHITE.

This form of carbon is known also as plumbago or black lead. It is found in many localities, but the largest deposits are in Ceylon and Siberia. There are also very considerable deposits in the United States.

Very pure graphite is now made in large quantities by the action of high temperatures on other forms of carbon in the electric furnace. A well known product of this sort is made at Niagara Falls.

Properties. Although a variety of carbon, this substance oxidizes with extreme difficulty. When heated in the air or oxygen it undergoes but little change, but certain oxidizing agents attack it at a high temperature. It has a specific gravity of 2.25 in pure form and is a moderately good conductor of heat and electricity.

Uses. Because of its very imperfect combustibility and infusibility, graphite is largely used in the manufacture of the so-called plumbago or black-lead crucibles employed in many industries, especially in the production of crucible steel. The graphite for this purpose is mixed with sufficient clay to make it coherent. It is used in our common "lead" pencils and as a protective coating for iron; common stove polish is usually fine graphite. It is

frequently employed as a coating for gunpowder to render the grains impervious to moisture, and because of its unctuous property is often used as a lubricant instead of oil.

AMORPHOUS CARBON.

Charcoal, coke, lampblack, boneblack and hard coal are the important varieties of amorphous carbon. Charcoal and coke are distinguished by their combustibility, lampblack by its properties as a pigment, and boneblack as a filtering material for the clarification of many organic liquids. The preparation of charcoal and coke will be illustrated by experiments.

Experiment 136. Charge a small retort, consisting of a piece of iron gas pipe 20 Cm. long and 15 Mm. in internal diameter, and closed air-tight at one end by an iron plug, with shavings or fine splinters, and attach it to a delivery tube and receiver as shown in the figure. Heat strongly with a Bunsen burner.

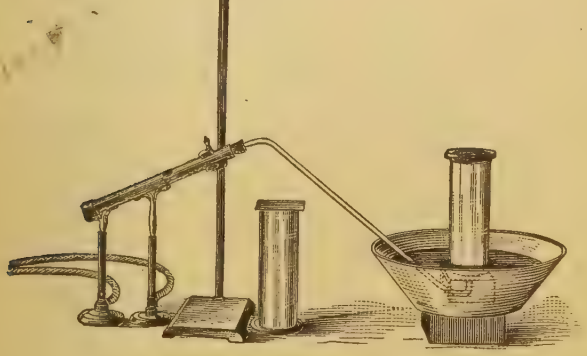

FIG. 22.

The wood is decomposed, and a mixture of water, acid liquids and gas passes over. The gas collects in the bottle, while the other substances condense. When the evolution of the gas has ceased, withdraw the delivery tube and then remove the lamp. After the iron tube has cooled shake out the contents, or remove them with a bit of wire, and test by burning. Close the mouth of the bottle with a glass plate, invert it and open to the air, and apply a match. The gas burns with a bright flame.

The process illustrated here is known as destructive distillation. Wood is a highly complex substance, containing a large amount of carbon. If heated in the air it *burns*—that is, it combines with the oxygen and is wholly consumed, yielding only gases and water vapor, with a minute trace of ash. But when heated to a high temperature away from the air, as in the above experiment, a very complicated reaction takes place, in which many products are formed. Besides carbon, the wood contains hydrogen and oxygen in large amount, and a little nitrogen. These elements combine with each other and with a part of the carbon to form new compounds, but the rest of the carbon is left in solid, nonvolatile form, and is called charcoal. A part of the liquid which distills in the above experiment forms a tarry substance on cooling, but as made here the amount is too small to be separated. Acetic acid, methyl alcohol or wood spirit, and acetone are other very important substances present in the products of the distillation, and on the large scale they are made by this process in quantity.

The gas collected in the bottles is called *wood gas*, and at one time was made for illuminating purposes by distilling wood in large retorts.

On the large scale in the manufacture of charcoal, wood is heated in large iron or brick retorts, or it may be cut up into cordwood lengths, stacked in circular heaps, covered with a thin layer of earth or sods and ignited at openings left at the base of the heap. A hole left at the top of the heap permits a slow circulation of air from which a partial combustion follows; a little of the wood is consumed, furnishing heat enough to char the rest.

Experiment 137. Repeat the last experiment, using soft coal in small lumps instead of wood. *Coke* remains in the tube, while a gas similar to ordinary illuminating gas collects in the bottle and can be tested as before.

In the dry distillation of the soft coal, the gas obtained burns with a better illuminating flame than that obtained in the other case. Coal differs from wood in containing more carbon and much less oxygen, from which it follows that the products of the distillation of coal must be char-

acterized by a lower percentage of oxygen. Some of these will be described later; we are at present concerned with the residues left in the retort. We have here two valuable varieties of amorphous carbon, which are produced on the large scale in enormous quantities, to be used for several purposes.

Ordinary charcoal, when freshly heated, has a marked power of absorbing gases, and hence is sometimes used for purifying contaminated atmospheres. It absorbs many solid substances also, and for this reason is employed in the construction of filters for the filtration of water. The value of charcoal for this purpose is by no means as great as was at one time supposed. Charcoal and coke are mainly used, however, in the smelting or reduction of ores, that is, in the operations in which certain metals are freed from the substances combined with them in their ores. The very marked affinity of carbon for oxygen comes in play here.

Boneblack, or bone charcoal, is an impure form of carbon left in the dry distillation of bones. It is employed mainly in the clearing of turbid or colored organic liquids, which can be illustrated by this experiment:

Experiment 138. Pour some water strongly colored with indigo solution into a porcelain dish and add half its volume of boneblack. Boil the mixture and then throw it on a paper filter. The liquid which runs through will be found colorless or nearly so. The experiment may be made also in this manner: Place a paper filter in a small funnel and half fill it with the boneblack. Now pour the liquid through and repeat this operation several times until the color is removed.

The rapidity of the absorption of coloring substances is greatly accelerated by heat, but on the large scale colored sugar syrups and other liquids are decolorized by forcing them through long columns of the boneblack packed in iron cylinders. The animal charcoal removes not only the coloring matter but many other objectionable substances as well. This form of carbon is frequently used in the laboratory for the purification of organic substances under preparation.

Lampblack is the carbon which separates from the smoke produced in the imperfect combustion of gases

and vapors. To secure the lampblack in quantity it is simply necessary to limit the supply of air so that the combustion must take place slowly and incompletely. Crude turpentine, pine knots, rosin and natural gas are all utilized in this industry. The carbon, being deposited from the condition of a gas or vapor, and not left as a residue as in the case of charcoal, boneblack and coke, remains in an extremely fine state of subdivision, and on this its value as a pigment largely depends. It is likewise quite insoluble in water or other liquid.

Coal exists in several varieties distinguished mainly by their proportion of carbon. All kinds of coal were formed by the slow decay of vegetation in absence of air, and in this decomposition the original vegetable matter lost a great deal of its nitrogen, hydrogen and oxygen, leaving a more or less pure carbon residue. Anthracite, or hard coal, is the variety richest in carbon; bituminous or soft coal contains carbon mixed with very complex hydrocarbons. Many grades of soft coal are known, some being much more valuable than others. Cannel coal may be mentioned here as a soft coal rich in volatile matter which burns with a bright, yellow flame. The following short table gives the average composition of the important kinds of coal. The original wood is added for comparison, and peat also, because it is a stage in the formation of many coals. The ash is deducted in the analyses.

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.
Wood	50.2	6.1	43.7	
Peat	61.5	5.7	32.8	
Lignite	67.9	5.7	25.4	1.0
Bituminous	79.4	5.3	13.9	1.4
Cannel	83.0	7.5	8.5	1.0
Anthracite	92.4	3.5	3.0	1.1

When anthracite is burned little beyond carbon dioxide is formed, while with wood and the softer kinds of coal a great deal of water is produced also.

CARBON AND OXYGEN.

The combination of carbon with oxygen has been illustrated in our experiments on oxygen. Two different compounds of these elements, both gases, are known, one called carbon monoxide, and represented by the formula CO, while the other is called carbon dioxide and is represented by the formula CO_2. The second is the most important and will be described first.

Carbon Dioxide.

While this substance is easily made by the combustion of carbon in oxygen it is best prepared for laboratory uses by the decomposition of a *carbonate*, or combination of carbon and oxygen with a metal. The most convenient carbonate we can use for this purpose is limestone, or the allied substance, marble.

Experiment 139. Arrange the apparatus as used in the production of hydrogen sulphide and charge it with small pieces of soft marble or limestone. Pour water through the funnel-tube and then some hydrochloric acid. The delivery tube leads into a dry, empty bottle. As the product is a gas much heavier than the air, it can be readily collected by displacement in this manner. The acid acts on the marble or limestone immediately, decomposing it and leaving a compound, called calcium chloride, in solution. The gaseous carbon dioxide escapes by the tube and enters the bottle, forcing out the air. Collect several bottles of the gas, and then put under the delivery tube a bottle containing about 50 Cc. of distilled water, to which about an equal volume of clear lime-water is added. Allow the gas to bubble into this while that in the bottles is tested.

Experiment 140. Add to one of the bottles some lime-water and shake thoroughly. A white precipitate forms which does not disappear on shaking. Dip a small lighted taper into a second bottle and notice that it is speedily extinguished. By means of a piece of wire hold a burning match or a small taper in the bottom of a clean bottle and *pour* into this the gas from a third collecting bottle. The light will be extinguished here as before. In a fourth bottle plunge some burning sulphur in a deflagrating spoon.

By examination of the solution left in the generating bottle and the amount of gas obtained, we are able to

write this equation as illustrating the decomposition of the marble:

$$\underset{\text{Calcium carbonate}}{CaCO_3} + 2HCl = \underset{\text{Calcium chloride}}{CaCl_2} + CO_2 + H_2O$$

One hundred parts of marble yield forty-four parts by weight of the gas. On bringing the gas into contact with the lime-water a white precipitate forms at first, as shown by one of the experiments, but if a large *excess* of the gas is passed into this turbid liquid the precipitate formed disappears almost completely. We have here two distinct reactions. In the first a certain amount of the gas combines with lime-water to produce a precipitate which on examination is found to be identical in composition, though not in external appearance, with the marble used in making the gas. The lime-water contains a substance known as calcium hydroxide, about which more will be said later. The combination between the calcium hydroxide, CaO_2H_2, and the carbon dioxide is represented by this equation:

$$CaO_2H_2 + CO_2 = CaCO_3 + H_2O$$

Here, as in other reactions we have had, a base and an acid substance unite to form a salt. Calcium carbonate is decomposed much in the same manner in which potassium nitrate and sodium chloride were decomposed by sulphuric acid.

The experiment of passing an excess of gas into the lime-water mixture, followed into its second stage, leaves a nearly clear solution. A simple explanation of this phenomenon may be given. The carbon dioxide in presence of water acts as a weak acid, which finally dissolves the precipitated calcium carbonate, making a new *soluble* substance known as calcium *bicarbonate*. The solution in the bottle, therefore, contains this substance. Pour out some of it into test-tubes and make the following experiments:

Experiment 141. To a small portion of the solution of calcium bicarbonate, just described, add some hydrochloric acid. Gas

bubbles escape, showing the decomposition of the substance in solution. Boil another portion in a test-tube and observe that gas escapes here also, while a precipitate forms. In this case heat decomposes the bicarbonate, driving off the excess of absorbed gas and leaving the ordinary insoluble carbonate.

These experiments illustrate some very common phenomena. Lake, river and well waters contain, often, calcium bicarbonate, formed by the solvent action of the carbon dioxide of the air, carried down by the rain water, on limestone rocks. Such waters are called *hard*. When they are boiled the bicarbonate is decomposed and a precipitate of carbonate produced. In boilers and teakettles this precipitate collects as a crust or scale.

Carbon dioxide is somewhat soluble in water, forming a weak solution of carbonic acid. It is absorbed by alkali solutions, forming carbonates.

Experiment 142. Lead the gas from the generator into a flask containing about 150 Cc. of distilled water. After fifteen or twenty minutes remove this flask and dip the delivery tube into a bottle or flask containing a weak solution of sodium hydroxide. Observe that the gas is much more perfectly absorbed here than in the water. Of the aqueous solution now pour about 10 Cc. into a test-tube and add some lime-water. A precipitate forms. Place the flask with the remainder of the solution on a sand-bath or gauze, heat slowly and then boil ten minutes. During the slow heating it will be noticed that gas bubbles collect along the sides of the flask and then escape. When the water actually boils the gas bubbles pass up rapidly. When no more are seen to escape allow the water to cool and to some of it add lime-water as before. A precipitate fails to form now, showing the absence of carbon dioxide. Next treat a portion of the solution of sodium hydroxide, into which the gas was passed, with hydrochloric acid; an evolution of gas is produced. Boil the remainder and add hydrochloric acid to it. We notice here, also, an evolution of gas, showing that heat does not drive it from the alkali solution, as it did from the water.

The tests just made should be thoroughly understood. We illustrate by this equation the formation of the weak acid produced when the gas is passed into distilled water:

$$CO_2 + H_2O = H_2CO_3$$

The carbonic acid, like sulphurous acid and ammonium

hydroxide, is not stable, but is decomposed by heat. Hence, when we boil its aqueous solution it soon disappears. With the sodium hydroxide, on the other hand, it forms a stable compound called sodium carbonate, having the composition Na_2CO_3, as illustrated in this manner:

$$CO_2 + 2NaOH = Na_2CO_3 + H_2O$$

This sodium carbonate is decomposed by hydrochloric acid just as the marble dust was above. Carbonates in general are decomposed by hydrochloric acid.

Still another source of carbon dioxide must be examined. It has been shown that it is produced in combustion processes where carbonaceous matter is burned. Ordinary wood and coal burned in a stove or furnace give rise to this gas. Now in the animal body a kind of combustion is in progress all the time, and as a result of this combustion, as of all others, heat is given off. The warmth of the body is derived from the oxidation or burning of the substances taken as food, all of which contain carbon. The most important product of this destruction of the food stuffs, or of the tissues built up from them, is carbon dioxide, and this leaves the body by the agency of the lungs in the breath, or expired air. We may test for it and readily recognize it.

Experiment 143. Pour some clear lime-water in a beaker and blow into it through a glass tube dipping beneath its surface. The liquid becomes turbid as before. After the action has been continued some minutes add hydrochloric acid to the contents of the beaker. The liquid becomes clear, while gas escapes.

This carbon dioxide thrown off from the lungs plays a very important part in nature. From this source, and from the combustion of fuel, enough enters the atmosphere to make about 3 volumes in every 10,000. The *total* amount in the air is very large. Were it not for the action of plants in absorbing the gas, in taking up and using as a food what animals reject, the air might in time become unfit for breathing. The presence of the gas in the air can be readily shown by exposing a little clear lime-water in a beaker to its action during ten or fifteen

minutes. In the atmosphere of a close, occupied room the lime-water becomes turbid very soon. In the outside atmosphere a longer time is required.

Carbon dioxide is formed also in the process known as alcoholic fermentation which will be fully described later. The amount of the gas liberated in this manner is enormous and, until recently, was allowed to go to waste. In many large breweries at the present time it is saved.

Physical Properties. One liter of carbon dioxide at standard temperature and pressure weighs 1.98 Gm. Referred to air it has a specific gravity of 1.529. At temperatures below 30.9° it may be condensed to a liquid which has a specific gravity of about 0.995 at 10°. The gas is soluble in water, one volume of which at 0° dissolves 1.797 volumes of the gas, while at 15° 1.002 volumes are dissolved and at 20° 0.901 volume.

Uses. Liquid carbon dioxide is now a common article of commerce. It is sold in strong steel cylinders and is employed for charging "soda" fountains, for extinguishing fires, for freezing and for several minor purposes.

The Carbonates. Carbon dioxide in water forms carbonic acid, which, however, is very weak and unstable. The salts corresponding are the common carbonates, some of which are readily decomposed by heat with loss of CO_2, while others are stable. Because of this weak nature of carbonic acid the alkali salts undergo hydrolysis in water, with production of an alkaline reaction. More will be said about this later.

Tests for Carbonates.

All carbonates are decomposed by mineral acids with evolution of CO_2. This is best recognized by the lime-water test given above. It has no odor and in this respect also differs from SO_2. Like the latter gas, it possesses the property of extinguishing flames.

Carbon Monoxide.

This oxide of carbon is a very important substance which differs from the other in essential properties. It is

not a natural substance, but can be produced by several reactions, one of which is here given:

Experiment 144. Powder 10 or 15 Gm. of potassium ferrocyanide, $K_4Fe(CN)_6$, place it in a flask of 300 Cc. capacity, having a funnel-tube and delivery tube. Add ten times its weight of strong sulphuric acid and heat gently on a sand-bath. The delivery tube should pass under water. Carbon monoxide is given off when a sufficiently high temperature is reached, and may be collected in bottles, as with hydrogen. Care must be taken to avoid applying too much heat, as the reaction would become very violent, and it should be remembered that the gas must not be inhaled, as it is poisonous. Collect several bottles of the gas and test them as follows: To one add lime-water; no precipitate results. Touch a lighted taper to another; the gas burns with a blue flame. Pour lime-water into the bottle in which this combustion took place, and notice that a precipitate now forms, showing that in the combustion carbon dioxide is produced. This experiment should be made in a fume closet.

The reaction between the ferrocyanide and sulphuric acid is somewhat complex, but its essential features may be written in this manner:

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 6CO + 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4$$

The six molecules of water represented come from the crystallized ferrocyanide and the commercial acid. Carbon monoxide is made very readily by the decomposition of oxalic acid, which is easily brought about by heating with strong sulphuric acid:

$$H_2C_2O_4 = H_2O + CO + CO_2$$

The sulphuric acid acts merely as a dehydrating agent to separate the elements of water. The evolved gas is passed through a wash bottle containing solution of caustic alkali to absorb the carbon dioxide, leaving the monoxide practically pure.

The gas is easily made by passing a current of the dioxide through a hot porcelain or iron tube filled with bits of broken charcoal. If the temperature is high enough a reduction takes place in this manner:

$$CO_2 + C = 2CO$$

The heat of an ordinary combustion furnace is sufficient for the reduction. This reaction is one which takes place in the blast furnace when iron ores are smelted and also in an ordinary coal fire. The blue flame seen above the coal is that of the burning CO. At the base of the stove or furnace CO_2 is produced to be decomposed above by the excess of carbon. In processes of incomplete combustion, where carbon burns in a limited supply of air, for instance, the gas is often formed. It is present in ordinary illuminating gas and is the chief substance which gives to this gas poisonous properties. It escapes sometimes from stoves with a coal fire, when the exit for the products of combustion is insufficient.

Properties. As shown above, the gas burns readily with oxygen. It is but slightly soluble in water and does not combine with alkali solutions as the dioxide does. It possesses the very important property of forming a peculiar stable compound with the hemoglobin of the blood, which greatly interferes with the oxygen-carrying power of the latter, and to this its marked poisonous action is due. The gas is free from odor when pure; it has recently been condensed to a liquid by application of pressure at a low temperature. One liter of the gas under normal conditions weighs 1.25 grams.

ILLUMINATING GAS.

Brief experiments given above illustrate the production of gases by the dry distillation of wood and coal. On the large scale both substances have been employed in the manufacture of gases for illuminating purposes. At the present time two general processes are in use for the production of gas for heating and lighting. These will be briefly described. In one case soft coal is distilled in large retorts and this process is now known as the "old gas process," while in the other case steam is decomposed by hot carbon under certain conditions, and this in various modifications is known as the "new gas process."

Old Process. The details of this are best explained with reference to the illustration, Fig. 23.

The retorts, of which several are built in a "bank" over one furnace, are shown at C; they are charged with

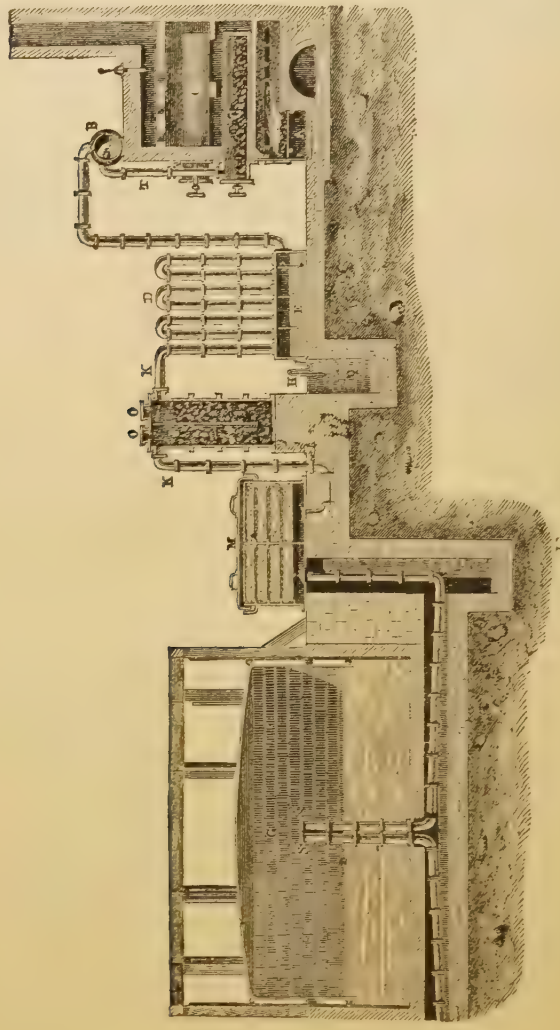

FIG. 23.

soft coal and closed by luted doors. The fire on the grate, A, brings the coal in the retorts to the point of decomposition. The hot gases and vapors pass up through vertical pipes connected with the front of each retort and enter a large pipe known as the hydraulic main. This hydraulic main, B, is half filled with water through which the gases must bubble. This water serves several purposes, one of which is to prevent ingress of air to the system when the retorts are opened from time to time to receive fresh charges of coal. After leaving the hydraulic main the gas passes through a series of pipes known as condensers, where it is cooled considerably and loses a large part of the tarry matter brought over from the retorts. This tar and condensed water run into a well through a trap, H. Then the gas goes through a coke tower called the scrubber, to be further freed from tar and ammoniacal salts by means of water trickling over the coke. Beyond the coke tower the gas enters another purifying appliance which is essentially a large box containing a number of trays filled with lime. The gas in passing back and forth over this lime gives up a large part of the hydrogen sulphide and carbon dioxide contained in it and is then ready for burning. From the lime box it passes by the pipe S to the gas holder G, and then to the city mains by the pipe S′.

The student will understand that this illustration is merely a diagram, showing the essential steps in the process only. The hydrocarbon gases, as liberated in the retorts, are mixed with sulphur compounds from the ferrous sulphide in all soft coal, and with ammoniacal salts from the nitrogen and oxygen in the coal. A large amount of tar is always formed, and these several impurities must be removed before the gas is suitable for burning in houses. The purification of the product is therefore the most difficult part of the process, and various appliances have been introduced for the purpose, but their important characteristics are shown above. The tar which condenses in different parts of the plant is saved and distilled. Among the valuable products obtained in the distillation are benzene, toluene, phenol, naphthalene and anthracene, which

are largely used at the present time in the manufacture of compounds valuable in medicine, in the arts as dye-stuffs, and elsewhere. Most of our ammonia and salts of ammonium are obtained from the wash waters of the gas works, and finally the coke left in the retorts after the completion of the process is employed as a valuable fuel. The average composition of the purified gas as made from soft coal, in different plants, is shown by the following table, the gas being considered in the dry condition:

	1	2	3	4
Hydrogen	46.2	39.8	51.3	46.0
Methane	34.8	43.1	36.5	39.5
Carbon monoxide	8.9	4.7	4.5	5.0
Heavy hydrocarbons	6.1	4.8	4.9	5.9
Carbon dioxide	1.5	3.0	1.1	1.2
Nitrogen	2.1	4.6	1.4	1.9
Oxygen	0.4	.....	0.3	0.5

For many years all the illuminating gas made in this country was produced essentially by this method, but since 1878 another general process has come into favor by which the larger part of the gas consumed in cities is now made.

The Water-Gas Process. While many kinds of plants are employed in practice, the foundation principle in all the newer methods is this: At a high temperature steam is decomposed by carbon with formation of hydrogen, carbon monoxide and carbon dioxide, the proportions of the last two depending on the temperature and excess of steam. We have these reactions:

$$H_2O + C = H_2 + CO$$
$$2H_2O + C = 2H_2 + CO_2$$

In practice anthracite coal is brought to a white heat in a retort by the aid of a blast of air. When this stage is reached the air is shut off and live steam blown in. This acts on the coal, yielding the products named. The gase-

ous mixture on leaving the retort passes through cooling and washing pipes and through lime boxes for the absorption of the carbon dioxide. What is left is nearly pure hydrogen and carbon monoxide and constitutes what is known as pure water gas or fuel gas. It burns with a blue flame, and has been employed for heating and to some extent for illumination by the aid of a special burner which becomes incandescent under the action of the burning gas. But most of the product is "carbonized" or "enriched" as made, and furnished directly as an illuminating gas. To accomplish this various methods have been patented. They amount essentially to this: A stream of light petroleum is injected into the retort in which the first reaction takes place or into a connected following chamber, called a "superheater," through which the hot gases pass. In either case the petroleum is decomposed by the high temperature, yielding permanent, light, gaseous products very similar to those found in the soft coal gas. Any excess of the oil not decomposed condenses in the cooling pipes and scrubbers and has no further action. In its composition water gas is mainly distinguished from soft coal gas by containing less methane but a much larger amount of carbon monoxide. When inhaled it is therefore more rapidly fatal, but otherwise in many respects is superior to the soft coal product.

Of the many minor processes employed locally in production of gases for lighting no mention need be made here, as they have little technical importance.

Gas Burners. Gas is used for two essentially different purposes; first, for the production of light, and secondly for heating. The illuminating burner is so constructed that air is mixed with the gas at the point of combustion only. The combustion takes place from the outside and is relatively slow. A part of the carbon is thrown into the reduced or free condition, and, becoming incandescent, makes the flame luminous.

In burners employed in heating, air is drawn into the gas stream by some device before the point of combustion is reached. This air mixes thoroughly with the gas and

with the aid of the outside air provides oxygen enough for perfect and rapid combustion of the carbon as well as hydrogen present. As no free carbon is produced here we have no incandescence. The common Bunsen burner was the first and is still the best illustration of this class of devices.

For the production of higher temperatures than can be secured by ordinary combustion the blast lamp is employed. In this a current of air or oxygen is blown by a bellows or otherwise into the center of the gaseous stream so as to hasten the oxidizing action. The best effect is obtained with pure hydrogen and oxygen, but oxygen and coal gas are very commonly used, as in the production of the calcium light. In the laboratory blast lamp air is blown into the common coal gas.

In recent years another form of lamp has become common, and in this the illumination is secured by the incandescence of a gauze cylinder or cone made of the oxides of several rare metals. A flame resembling the Bunsen flame plays against this gauze cylinder, bringing it up to the white hot condition when it emits a very brilliant light. The material of the gauze cylinder consists usually of a mixture of the oxides of thorium, cerium and other rare metals. These oxides become incandescent at a relatively low heat. Lime becomes incandescent when heated in the oxyhydrogen flame, and the light so produced is called the calcium light, lime light or Drummond light.

Safety Lamp. It is a matter of common observation in the laboratory that the Bunsen burner flame may appear above wire gauze and not strike through, and also that when burning below it is often unable to pass through and burn above. The explanation of this is found in the fact that the gauze is so perfect a conductor of heat that the temperature of the combustible gas on the opposite side of the gauze from the flame does not reach the kindling point. This is easily shown by lamp flames as well as with those from gas. The principle was recognized and explained by Humphrey Davy and applied by

him in the construction of the safety lamp. This is an oil lamp with a chimney of fine iron gauze. The top and bottom of the chimney are not open, but made of gauze so that the flame is surrounded. When the lighted lamp is taken into a mine containing marsh gas this passes with the air through the meshes and causes a slight explosion. But the conducting power of the wire keeps the temperature of the burning gas below the point at which the explosive mixture outside could be ignited, giving the miner time to seek a place of safety. The lamp gives a warning of the presence of marsh gas; if kept burning long enough in such an atmosphere the gauze chimney may in time become hot enough to communicate the combustion to the outside.

CARBON AND HYDROGEN.

Many hundreds of compounds of these elements are known, some of them being natural products, while others are made by laboratory operations. They are called *hydrocarbons*. Ordinary crude petroleum consists essentially of bodies of this class, while other natural substances contain them also. The part of chemistry known as organic chemistry is concerned with a study of these substances and others related to or derived from them. A few will be studied here as illustrations.

Methane or Marsh Gas.

This is a light, gaseous body, containing 75 per cent of carbon and 25 per cent of hydrogen by weight. It is found in the gases escaping from oil wells and makes up a large proportion, often 95 per cent, of the so-called natural gas found in many parts of the country. It is often given off from marshy ground or stagnant pools, hence the name, and is formed there by the decay of organic matter. In the laboratory we can make it by the following method:

Experiment 145. Prepare a mixture of 1 part of thoroughly dried (dehydrated) sodium acetate and three parts of soda-lime. Charge about 20 Gm. of this into a gas-pipe retort arranged as in the experiments on the production of coal and wood gases.

When a strong heat is applied to the retort a decomposition of the mixture takes place and methane is given off. This is collected over water. Fill one or two bottles and test. The gas burns with a bluish flame if pure, but as here made has often a yellowish color from the presence of sodium compounds carried over in traces from the mixture in the retort. The gas is very light and can be poured upward, as was hydrogen. Test with lime-water for carbon dioxide among the products of combustion, when the gas is burned.

Methane is a constituent of illuminating gas, amounting often to 40 per cent. of the whole by volume. It collects sometimes in deep coal mines and is there known as *fire damp*, giving rise frequently to violent explosions.

The reaction which takes place when methane is made by the above process is this:

$$\underset{\text{Sodium acetate}}{NaC_2H_3O_2} + \underset{\text{Sodium hydroxide}}{NaOH} = \underset{\text{Sodium carbonate}}{Na_2CO_3} + \underset{\text{Methane}}{CH_4}$$

The sodium hydroxide is contained in the soda-lime. When methane burns, water and carbon dioxide are formed as here illustrated:

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

One volume of methane requires two volumes of oxygen for complete combustion, or ten volumes or air. The gas is insoluble in water, practically, and is not absorbed by alkali solutions.

Ethylene.

This a colorless gas which is formed in small quantity in illuminating gases. In the laboratory it is most readily made by heating a mixture of alcohol and strong sulphuric acid.

Experiment 146. Pour about 20 Cc. of alcohol into a flask of 300 to 400 Cc. capacity and add, a little at a time, and with agitation of the flask, about 80 to 100 Cc. of strong sulphuric acid. Close the flask with a stopper carrying a safety tube and a delivery tube. Lead the latter into a Woulfe bottle as in the experiment on the production of HCl. In the present case half

fill the first bottle with sulphuric acid, into which the delivery tube dips, and the second bottle with a solution of sodium hydroxide. Now heat the flask on a sand-bath very gradually until the evolution of gas begins, as shown by the rapid escape of bubbles through the alkali solution. Then regulate the flame so as to prevent too rapid a reaction in the flask, as this would lead to frothing of the liquid, and overflow through the funnel tube and delivery tube. Remove the lamp entirely if necessary. As generated, the gas is not pure but on passing through the acid of the first bottle and the alkali of the second it gives up most of the contaminations, consisting mainly of carbon dioxide, sulphurous oxide and ether vapor. From the second Woulfe bottle a delivery tube leads to a trough holding inverted bottles full of warm water for the collection of the gas. Fill two or three bottles and test the gas by burning it. After lighting the gas at the mouth of a bottle pour water through the flame to force the gas up to the air more rapidly. A bright illuminating flame is produced. The gas may also be burned at the end of the delivery tube, or after passing through a common lava gas tip.

This gas, although being present in but small proportion in common illuminating gas, is important because of its light-giving property. Hydrogen, methane and carbon monoxide make up about 85 to 90 per cent. of the volume of our common gas, but burn with nonluminous flames. Ethylene and several other gaseous substances present in small amount burn with highly luminous flames and are valuable on that account.

It has been shown that sulphuric acid has a marked affinity for water and that it can even decompose organic substances to combine with it. The decomposition of alcohol is an illustration of this. Alcohol is a compound of carbon, hydrogen and oxygen having the formula C_2H_6O. The strong acid decomposes this, taking out H_2O and leaving C_2H_4:

$$C_2H_6O - H_2O = \underset{\text{Ethylene}}{C_2H_4}$$

Acetylene.

This is another interesting compound of carbon and hydrogen, with the composition expressed by the formula C_2H_2. It is found in illuminating gas and is made in

processes of imperfect combustion of some other gases or vapors. Recently it has received much attention from chemists because of the fact that by a new method it can be produced at small cost and in any desired quantity. As it is a highly valuable illuminant this discovery is of importance. It is made in this new process by the decomposition of a compound known as calcium carbide, by means of water. An experiment will show this.

Experiment 147. Arrange a bottle exactly as for the generation of hydrogen. The bottle should have a capacity of about 150 Cc. Put 15 to 20 Gm. of the calcium carbide in the bottle and add strong alcohol to make a layer about 1 Cm. in depth. Close the bottle with the cork, holding a funnel-tube and a delivery tube, the latter leading to a trough with inverted collecting bottles. The lower end of the funnel-tube should dip below the surface of the alcohol. Now pour in a little water slowly and continue the addition until a rapid evolution of gas begins. Allow the first portions to escape into the air and then collect some for tests. Notice that it burns with a heavy, smoky flame. If the gas is burned through a lava gas tip, it is bright and luminous. Lead a little of the gas from the generating bottle into a flask containing a solution of cuprous chloride in ammonia water. A characteristic red precipitate is formed.

The gas has a peculiar disagreeable odor and is poisonous when inhaled in quantity. The reaction by which it was formed is illustrated as follows:

$$\underset{\text{Calcium carbide}}{CaC_2} + 2H_2O = \underset{\text{Calcium hydroxide}}{CaO_2H_2} + \underset{\text{Acetylene}}{C_2H_2}$$

Acetylene may be condensed to the liquid condition without practical difficulty and to some extent is used in that form. It is preferable and safer, however, to burn it as generated, at the ordinary pressure. The carbide from which it is made is a good illustration of a class of substances which have recently been made in quantity by aid of the high heat of the electric arc. In this case a mixture of powdered coke and lime is exposed to the heat of the arc with the formation of carbide and carbon monoxide.

$$CaO + 3C = CaC_2 + CO$$

CARBON, HYDROGEN AND OXYGEN.

These compounds, like those of carbon and hydrogen alone, are very numerous. The starches, sugars, gums, resins, alcohols, fats and many other common substances contain these three elements. At one time it was supposed that these bodies could be produced only by the agency of living plants or animals. We know now that this is not true, as many combinations of these three elements are easily made by laboratory operations. A few simple illustrations will be given here of the preparation and properties of some so-called organic substances. Starch will be taken as the starting point, as it is a common substance and is used for many purposes.

Experiment 148. Rub about 10 grams of starch to a thin cream with a little water. Then add water to make a volume of about 200 Cc., and boil the mixture to form a paste. Add now 5 Cc. of dilute sulphuric acid and boil three hours, or more, in a flask. Add a few drops of hot water, from time to time, to compensate for that lost by evaporation. At the end of the boiling it will be noticed that the mixture is clear, the starch having been dissolved. Next add to the hot liquid some fine marble dust and shake the mixture thoroughly. Continue the addition as long as carbon dioxide is given off, by the action of the free sulphuric acid on the calcium carbonate. The object of adding the marble dust is to neutralize the acid. Allow the mixture to cool, dilute it with some water, and filter it into a clean beaker. If the filtrate has an acid taste add a little more marble dust to it, warm, allow to settle, and filter again. Evaporate this filtrate to dryness, best over a water-bath. At any rate the temperature must not get high enough to scorch the substance as it becomes concentrated. From time to time take up a drop of the liquid on a glass rod, cool and taste it. By the action of the sulphuric acid on the starch a sugar, known as *dextrose* or *glucose*, is produced. The acid itself is but slightly altered in the process; most of it remains until the end of the boiling, and then it is combined with the marble dust to form insoluble calcium sulphate, which is removed in the filtration. The weak sugar solution is concentrated until its nature becomes apparent by the taste.

Starch is represented by the formula $C_6H_{10}O_5$, and the dextrose by the formula $C_6H_{12}O_6$. The weak acid has apparently added H_2O to the starch, which is a behavior quite the reverse of that of the strong acid, already shown.

The reaction illustrated here is identical with one followed on the large scale, in which commercial *glucose* is made by heating starch paste with weak sulphuric acid, in closed vessels under steam pressure.

To show some of the properties of the sugar formed in the experiment dissolve it in water and test the solution.

Sugar Tests. We have several very sharp reactions by which we are able to recognize dextrose in a solution. One of the best of these will be given here.

Experiment 149. Add to a few Cc. of the sugar solution an equal volume of strong potassium hydroxide solution, and then a few drops of a weak solution of copper sulphate. A blue color appears, much deeper than that of the copper sulphate. Now boil the liquid. On heating, it becomes turbid and greenish yellow. A precipitate forms which darkens and becomes heavier until at the boiling temperature it is bright red. This precipitate consists of a combination of copper with oxygen known as cuprous oxide, and represented by the formula Cu_2O. The sugar acts here as a *reducing* substance, but the nature of the reaction cannot be explained at this point. The test, as carried out here, is known as *Trommer's* test. A very similar behavior is shown on boiling the sugar solution with *Fehling's* solution, which also contains copper. The preparation of this solution is given in books on analytical chemistry. It is essentially a solution of copper hydroxide with an alkali and a tartrate.

These tests are characteristic of dextrose, and some other sugars, but not of cane sugar. When a solution of cane sugar is boiled with a weak acid, however, it is converted into dextrose and a similar substance known as levulose and this mixture responds to the test. Prove this by an experiment.

Experiment 150. Dissolve about 5 Gm. of pure cane sugar in water, in a clean test-tube. Divide the solution into two parts. Apply the *Trommer* or *Fehling* test to one of these and observe that no red precipitate is formed. Then boil the other half of the solution with a few drops of strong hydrochloric acid some minutes, add some alkali to neutralize the acid, and apply the test as given. A bright red precipitate appears almost immediately.

These tests are of the highest importance and are employed frequently in analytical chemistry.

The sugars are good illustrations of bodies which do not dissociate or break up into ions when dissolved. Such reactions as we find with salts, or bases, or acids are lacking with the sugars. They form a few "molecular" combinations, but these bear little relation to the ion combinations frequently referred to.

From starch we made dextrose by action of a weak acid and heat. It will next be shown how the sugar may be converted into something else of equally great importance. But for this we will need a greater quantity of sugar than was made in the above experiment. Common glucose syrup or molasses may be used for the purpose.

Fermentation. When a solution of molasses or glucose, not too concentrated, is mixed with a little yeast, or exposed some time to the air, it undergoes a change which we call fermentation. The solution becomes lighter, gives off a gas which we recognize as carbon dioxide, and emits the characteristic odor of alcohol. This change is produced by the agency of what is termed a ferment. There are several kinds of ferments; but the one concerned here, the yeast ferment, consists of minute vegetable cells which can be seen under the microscope. The function of these cells is to consume sugar and produce alcohol and carbon dioxide. The change will be shown by an experiment.

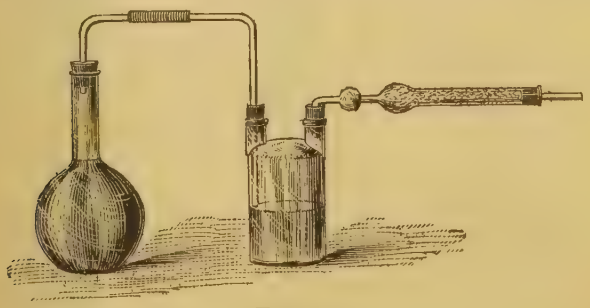

FIG. 24.

Experiment 151. Mix 100 Cc. of common glucose molasses with 800 to 900 Cc. of water, and with the mixture nearly fill a bottle or flask. Add 5 Cc. of brewer's yeast, or some compressed

yeast previously soaked in water. Close the bottle with a perforated stopper and connect it with a Woulfe bottle and soda-lime tube as shown in the last figure.

Half fill the Woulfe bottle with lime-water. Leave the apparatus two or three days in a moderately warm place. Active fermentation soon begins and bubbles pass over from the generating bottle into the lime-water, where a precipitate is soon formed. The alkali in the soda-lime tube serves to protect the lime-water from the carbon dioxide of the air at the beginning of the experiment. The precipitate which forms at first in the lime-water clears up later, as an excess of the gas passes through. At the end of three days disconnect the apparatus and use the liquid in the fermentation bottle, which is now a weak solution of alcohol, for the following experiments:

Experiment 152. Divide the fermented liquid into two halves. Allow the one half to stand some days in an open bottle, exposed to the air. With the other half proceed as follows: Fill it into a flask, as shown on the left in the figure below, and connect this with a second flask on a water-bath or dish of water. A delivery tube from this second flask leads in turn to a small, open flask, which may be kept cool by standing it in cold water.

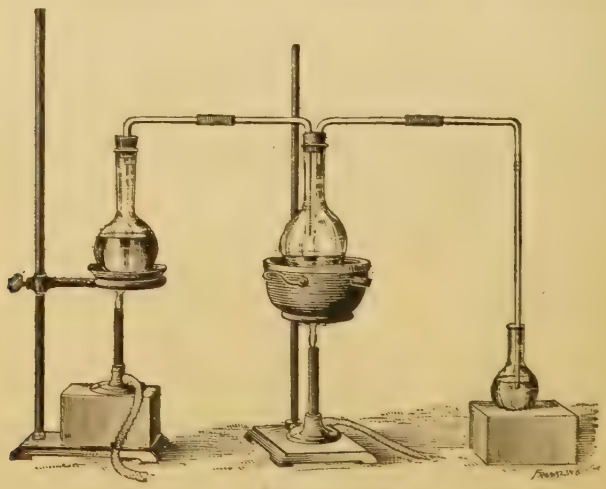

FIG. 25.

The first flask is heated on a sand-bath, so that the liquid in it just boils. The alcohol present distills with water over into the second flask. This is heated to a lower temperature in order

to distill, as far as possible, only the alcohol. As there is a difference of 20° C. in the boiling points of alcohol and water, a much stronger product may be driven over from the second flask than from the first. The distilled alcohol with water collects in the small flask, and may be tested by burning. At the end of the distillation, that is, after about a third of the contents of the first flask has been boiled over, pour some of the product from the small flask into a porcelain dish and apply a light. It should burn with a colorless flame.

On the large scale alcohol is produced by an analogous process, and is concentrated by distillation until it has a strength of about 93 per cent by volume. The proportions of alcohol and carbon dioxide obtained from the sugar are represented by this equation:

$$\underset{\text{Dextrose}}{C_6H_{12}O_6} = \underset{\text{Alcohol}}{2C_2H_6O} + \underset{\text{Carbon dioxide}}{2CO_2}$$

Alcohol is employed for many purposes in the laboratory and in the arts. It is used as a solvent in making varnishes, perfumes, etc., and also as the starting point in the manufacture of many other substances. Ether and chloroform are illustrations of bodies made from alcohol.

Acid Fermentation. We have yet the other half of our alcoholic liquid to examine. Allow it to stand in the air, as directed, until the odor of alcohol disappears and a *sour* odor takes its place. Under certain circumstances, on standing, alcohol becomes converted into acetic acid. The change is much more rapid if to it is added a little of the substance known as *mother of vinegar,* which, like the yeast, is a ferment. The alcohol ferment and the acetic acid ferment are present in nearly all atmospheres and bring about the production of alcohol, and then the change into vinegar, in fruit juices exposed to the air.

Experiment 153. Treat the alcoholic liquid, which has become sour, in this manner: Filter it first and to the clear filtrate add a few grams of marble dust. A slow solution of the solid will be observed, as the acid liquid forms with it soluble calcium acetate, with escape of carbon dioxide. The solution is aided by heat. When no more marble dust dissolves filter the mixture and concentrate the filtrate on a water-bath, or sand-bath, slowly. On a sand-bath, care must be taken not to char the concentrated

product. When cold the nature of this may be readily recognized by adding a little strong sulphuric acid. This decomposes the calcium acetate, as it does other salts (chlorides, nitrates, carbonates, etc.), with liberation of acetic acid, which is recognized by the odor. The object of converting the acid in the sour liquid into calcium acetate is to secure a product which may be concentrated without loss and then be recognized. In the original liquid the acid is in a highly diluted condition, and not easily recognizable.

The composition of acetic acid is $C_2H_4O_2$, while that of the alcohol from which it was derived is C_2H_6O. The vinegar ferment, therefore, adds oxygen and abstracts hydrogen, but in what manner this is done we cannot explain. Acetic acid is an important substance, occurring to the extent of 3 or 4 per cent in ordinary vinegar. Vinegar and weak acetic acid, for certain purposes, are made by fermentation, but a great deal of our strong acid is obtained from the acid liquid produced in the distillation of wood, and known in crude form as pyroligneous acid. Acetic acid forms a class of salts known as *acetates,* of which we have had several illustrations.

CARBON AND NITROGEN.

Carbon and nitrogen enter into important combinations, one of which will be briefly referred to. This is *cyanogen* and is represented by the symbols CN. This cyanogen combines with metals, forming compounds known as cyanides. Potassium cyanide is an illustration. This has the composition KCN. In this group the carbon and nitrogen seem to have the effect of a single element, for instance chlorine. Potassium cyanide is in some respects analogous to potassium chloride. It goes into combinations with other cyanides very readily, yielding so-called double cyanides. The potassium-iron cyanides will be referred to later, as they are interesting and important compounds.

A solution of potassium cyanide is used in photography as a fixing agent because of its marked solvent action on silver chloride or bromide. The ordinary plating baths employed in gold and silver plating are usually made of the double cyanides of potassium and silver, and potas-

sium and gold dissolved with an excess of potassium cyanide. These solutions are intensely poisonous.

As a chloride is decomposed by sulphuric acid, yielding hydrochloric acid, so a cyanide may be decomposed, yielding hydrocyanic acid, HCN, as illustrated by this equation:

$$2KCN + H_2SO_4 = K_2SO_4 + 2HCN$$

Hydrocyanic acid is commonly known as prussic acid. It is a very volatile liquid, extremely poisonous, and may be handled with safety only in dilute solutions. It dissolves in water in all proportions. A fuller discussion of the cyanogen compounds belongs in the field of organic chemistry.

CARBON AND CHLORINE.

Carbon forms a number of important compounds with chlorine, or with chlorine and hydrogen, which are described in organic chemistry. The common substance known as chloroform has the formula $CHCl_3$. It is sometimes called trichlormethane and may be looked upon as marsh gas, or methane, in which three atoms of hydrogen are replaced by three chlorine atoms. Another compound has the formula CCl_4, and is called tetrachlormethane, or tetrachloride of carbon. Both are volatile liquids with a characteristic, pleasant odor and are employed in medicine as anæsthetics. In these halogen compounds the chlorine does not behave as an ion. It seems to be very firmly combined with the carbon, as silver nitrate will not separate it in the usual way.

CARBON AND SULPHUR.

Carbon forms a very important compound with sulphur, known as carbon disulphide, CS_2. It is produced by passing the vapor of sulphur over hot carbon in a retort. At the same time several other compounds are formed, some of which remain with the disulphide as contaminations hard to separate. Pure CS_2 is a liquid with a pleasant ethereal odor, boiling at 47° and having a density of 1.29. It is but slightly soluble in water, and is itself an excellent solvent for sulphur, caoutchouc, fats

and other substances. Because of this behavior it has many uses in the arts and in analytical chemistry. The common commercial disulphide has a very disagreeable odor due to the presence of the impurities formed in the process of manufacture. The vapor of carbon disulphide is very inflammable and is also poisonous when inhaled. Care must therefore be observed in handling it.

In its chemical behavior CS_2 bears some relation to CO_2. With the latter this reaction occurs:

$$Na_2O + CO_2 = Na_2CO_3,$$

and an analogous combination is known for the disulphide. Sulphide of sodium unites with it in this manner:

$$Na_2S + CS_2 = Na_2CS_3$$

The compound Na_2CS_3 is called sodium thiocarbonate, or sometimes sulphocarbonate. It may be decomposed by hydrochloric acid, yielding an acid, H_2CS_3, corresponding to the real carbonic acid, and called thiocarbonic acid.

CARBON AND SILICON.

Two compounds of these elements are known, the monocarbide of silicon and the dicarbide, SiC and SiC_2. The first of these is important under the name of carborundum.

Carborundum. This compound was discovered a few years ago and is made in the electric furnace by the action of coke, in powder, on silica. The temperature of the reaction is over 3000°.

$$SiO_2 + 3C = SiC + 2CO$$

The substance is a dark green crystalline mass which is distinguished by its extreme hardness. It is employed therefore mainly for grinding and polishing, and is made into grindstones and whetstones, and also into glass cutters. It is extremely insoluble and may be burned in oxygen only with difficulty. In 1903 the production in the United States was about 2,500 tons.

CHAPTER XII.

ATOMIC AND MOLECULAR WEIGHTS.

DALTON'S WEIGHTS.

In Chapter III a brief outline of the atomic theory as suggested by Dalton was given. It is intended in the present chapter to go a little more fully into details and explain some of the steps by which chemists have passed from the views of the earlier writers to those held at the present time.

It was Dalton's idea that where atoms combine to form compounds such combinations must be in the simplest possible proportions, an atom of one with an atom of the other in most cases. Giving hydrogen unit atomic weight, it would follow, therefore, that atomic weights would be found by determining the weights of different bodies which unite with one part of hydrogen.

Let M represent an atom of one substance and N an atom of another; then a combination between the two would be in the proportion:

$$x\mathrm{M} : y\mathrm{N},$$

with x and y generally 1. The atomic weights which Dalton actually found were inaccurate because of his faulty analytical methods, but his principle would lead to the following:

Water	$=$HO	H : O :: 1 : 8.00.	O $=$ 8.00.
Ammonia	$=$HN	H : N :: 1 : 4.67.	N $=$ 4.67.
Ethylene	$=$HC	H : C :: 1 : 6.00.	C $=$ 6.00.

If 8 parts of oxygen unite with 1 part of hydrogen and 4.67 parts of nitrogen unite with the same weight of hydrogen then it might be expected that when oxygen and

nitrogen unite with each other the proportion 8:4.67 would represent the relation of their weights. But this is not the case and the atomic weights as given appear inconsistent; it will be later seen that this is due to a false assumption regarding x and y in the proportion, $xM : yN$, above. The first atomic weights published by the followers of Dalton suffered many arbitrary corrections with the hope of making them consistent among themselves.

COMBINATION OF GAS VOLUMES.

Several chemists had undertaken to determine the proportions in which various gases unite with each other, but it remained for Gay Lussac to discover the extreme simplicity of these relations. It has been shown in an earlier chapter that 2 volumes of hydrogen unite with 1 volume of oxygen to form 2 volumes of water vapor. Through the labors of Gay Lussac and others a number of similar simple relations were established which are shown in the following short table:

2 vols. of hydrogen	+ 1 vol. of oxygen	= 2 vols. of water vapor.
3 vols. of hydrogen	+ 1 vol. of nitrogen	= 2 vols. of ammonia.
2 vols. of sulphurous oxide	+ 1 vol. of oxygen	= 2 vols. of sulphuric oxide.
2 vols. of nitrogen	+ 1 vol. of oxygen	= 2 vols. of nitrous oxide.

Somewhat later other very simple relations were found, among them these:

1 vol. of hydrogen	+ 1 vol. of chlorine	= 2 vols. of hydrochloric acid.
4 vols. of hydrogen	+ 1 vol. of carbon (assumed as vapor)	= 2 vols. of marsh gas.

Gay Lussac pointed out the fact that in all cases investigated the volume of product formed bears a very simple relation to the sum of the components. This is shown in the examples quoted.

The question was naturally asked: What is the reason for this combination of gases in simple volume propor-

tions? Answers of the highest importance in the history of chemistry were given in two directions. The first to correctly interpret the gas experiments of Gay Lussac, Humboldt and Davy was Amadeo Avogadro, a professor in the University of Turin. In 1811 he published an article in which he deduced from these experiments the law that *equal volumes of gases, under like conditions, contain the same number of particles or integrant molecules.* Unfortunately the value of the observation of Avogadro was not recognized for many years. More will be said about it presently.

THE VOLUME THEORY OF BERZELIUS.

Among the ablest chemical investigators working in the earlier years of the nineteenth century there must be mentioned Berzelius. At the time when Dalton announced his doctrine of combinations through atoms of constant weight Berzelius was already engaged in the analysis of chemical compounds, and, accepting Dalton's idea, he immediately began the task of fixing atomic weights by determining the proportions in which various substances combined with oxygen and hydrogen. Dalton had suggested hydrogen as the basis of atomic weights, but, inasmuch as the known oxygen compounds were more numerous than those of hydrogen and more readily examined, he proposed the oxygen atom as the unit and placed its weight arbitrarily at 100. In addition to this he announced two important principles to be employed in fixing atomic weight. One of these he derived from the discoveries of Gay Lussac and his followers just mentioned. Berzelius, like Avogadro, recognized immediately the great importance of these simple volume relations in the combination of gases. This was his interpretation of them. *To unite in this manner*, he reasoned, *equal gas volumes must contain the same number of atoms, under like conditions of temperature and pressure.* From this it would follow that the atomic weights of the gaseous substances must be related to each other as are their specific gravities. This he called his *volume theory* in atomic weight determination. It will be observed that

he made no distinction between elementary and compound gases, a distinction which was embraced in Avogadro's theory. Inasmuch as the density of oxygen was found to be about sixteen times that of hydrogen, it will be further noticed that the theory of Berzelius places the atomic weight of oxygen, referred to hydrogen, as 16:1 instead of 8:1, as in the Dalton system, the former assuming two atoms of hydrogen with one atom of oxygen in the water molecule while the latter assumed one atom of each.

To find the atomic weights of the nongaseous elements from their combining proportions Berzelius announced another principle, viz.: that *in all compounds of two elements one must be present as a single atom.* This rule, it will be recognized, is perfectly arbitrary, resting on no experimental basis. Yet by combining his two principles he was able to make many valuable determinations, some of which are still recognized as practically correct. In the cases of most of the metals, however, his first published atomic weights were twice as great as those now commonly accepted, and in fact twice as great as the weights he announced later himself. It should be said here that most of our present atomic weight values are based on the original determinations of Berzelius. It will be interesting to note the figures actually given by this writer in 1815 and 1826. In calculating his first table he made certain *assumptions* regarding the composition of the oxides which led him to the double values for the weights of the metals. In ferrous oxide, for example, he assumed a composition which we now express as FeO_2. Finding in this for 200 parts of oxygen 603.6 parts of iron, he considered this as representing the weight of one atom of the metal on his oxygen scale. This corresponds to an atomic weight of 111 on our present system. But giving to ferrous oxide the composition FeO, the weight would be reduced one half. The same explanations apply to the oxides of lead and copper and to other compounds which Berzelius worked with. Several years later, however, a new principle was discovered by Mitscherlich, as explained below, and this the Swedish chem-

ist accepted as of fundamental importance. He applied it to the correction of his weights, giving them the values now practically retained as correct.

In the following table some of the Berzelius atomic weights of 1815 and 1826 are given. Those of the latter year are reduced to the hydrogen scale, as shown in the fourth column, while in the last column our present values are given for comparison. The agreement is in most cases very close.

The Weights of Berzelius.

	1815.	1826.	1826 Reduced.	Present Values.
Oxygen	100	100	16.0	16.0
Sulphur	201	201.2	32.2	32.1
Phosphorus	167.5	196.2	31.4	31.0
Carbon	74.9	76.4	12.5	12.0
Hydrogen	6.64	6.24	1.0	1.0
Arsenic	839.9	470.0	75.2	75.0
Chromium	708.1	351.8	56.6	52.1
Tellurium	806.5	806.5	129.1	127.6
Antimony	1613	806.5	129.1	120.2
Platinum	1206.7	1215.2	194.5	194.8
Gold	2483.8	1243.0	198.9	197.2
Mercury	2531.6	1265.8	202.6	200.0
Silver	2688.2	1351.6	216.3	107.9
Copper	806.5	395.7	63.3	63.6
Nickel	733.8	369.7	59.2	58.7
Lead	2597.4	1294.5	207.1	206.9
Tin	1470.6	735.2	117.6	119.0
Zinc	806.4	403.2	64.5	65.4
Aluminum	343.0	171.2	27.4	27.1
Iron	693.6	339.2	54.3	56.0
Magnesium	315.5	158.4	25.3	24.4
Calcium	510.2	256.0	40.9	40.1
Strontium	1118.1	547.3	87.6	87.6
Barium	1709.1	856.9	137.1	137.4
Sodium	579.3	290.9	46.5	23.0
Potassium	978.0	489.9	78.4	39.1

It will be observed that most of the Berzelius weights in the above table of 1826 agree pretty well with those of the present time. The weights of sodium, potassium and silver are still twice as great as the modern values, how-

ever. Berzelius did not consider nitrogen and chlorine as simple substances and hence his atomic weights for them bear no simple relation to any now recognized.

Turner's Table.

Dr. Edward Turner, a contemporary of Dalton and Berzelius, published not a little on the subject of atomic weights. His results were partly of his own determination, but more largely based on the work of Dalton, Wollaston and Berzelius. Wollaston, like Dalton, took the relation of hydrogen to oxygen as 1 : 8, but assumed O = 10 as the basis of his system. In the American edition of Turner's Chemistry, published in 1822 and 1823, the author gives his own table in detail, with H = 1 as the basis of weights. A part of this table is here quoted for comparison with that of Berzelius.

"TABLE OF CHEMICAL EQUIVALENTS, OR ATOMIC WEIGHTS."

Hydrogen	1	Iron	28
Aluminum	18	Lead	104
Antimony	44	Magnesium	12
Arsenic	38	Mercury	200
Barium	70	Nitrogen	14
Bismuth	71	Oxygen	8
Cadmium	56	Phosphorus	12
Calcium	20	Potassium	40
Carbon	6	Silver	110
Chlorine	36	Sodium	24
Chromium	28	Strontium	44
Cobalt	30	Sulphur	16
Copper	64	Tin	59
Gold	200	Zinc	33

It will be noticed that many of the numbers in the above table are quite different from those given by Berzelius, which led to much confusion for many years. It is, however, easily recognized that by multiplying by 2 the weights of oxygen, carbon, sulphur, chromium, iron, lead, magnesium, strontium, barium, calcium, tin and zinc in the Turner table values very close to those of the Berzelius table are reached, which correspond to those now in use. Also, by dividing by 2 the weights for sodium, po-

tassium and silver as given by Berzelius, we obtain numbers agreeing well with those of Turner, accepted at the present time. It is evident, therefore, that these differences may be traced to fundamental differences in theories of combination rather than to differences in actual results of analyses. With the proper theory of the union of atoms to form compounds, it was recognized by these earlier chemists that their analytical results might be differently interpreted and brought into accord. Important aids in the choice of atomic weights were soon forthcoming.

THE LAW OF ISOMORPHISM.

In 1819 Mitscherlich published the important discovery that in many groups of crystalline compounds of like form certain elements may replace each other without causing essential change in the crystalline structure. Such bodies he described as *isomorphous,* that is, of like form. Thus, nickel, cobalt, zinc, iron and magnesium sulphates are formed by the solution of the metals or oxides in sulphuric acid, yielding salts which resemble each other in form and in the amount of water of crystallization held. In another class of sulphates, iron, chromium and aluminum replace each other perfectly. These metals are, therefore, isomorphous with each other in their compounds. Many of the salts of phosphoric and arsenic acids are found to crystallize in similar forms, and the metals in them may be considered as isomorphous. Now, it occurred to Berzelius and others, that in these cases the metals must replace each other in atomic proportions, and given the atomic weight of a metal in any one group of isomorphous substances, the other atomic weights might be found by a determination of the corresponding replacing weights. As a matter of fact, Berzelius employed the principle in many cases to correct his earlier determinations, and it is still of value in choosing between possible proportions found by analysis alone.

THE LAW OF DULONG AND PETIT.

In Chapter II a unit of heat was defined as the amount of heat required to raise the temperature of a gram of

water one degree centigrade. It was known to physicists before the end of the eighteenth century that very different amounts of heat are required to warm a gram of other substances through the same range of temperature. The *specific heat* of a substance may be defined as the fraction of a unit of heat necessary to raise the temperature of one gram of that substance through one centigrade degree. These specific heats are all fractions, with one exception, that of hydrogen. In other words, less than a unit of heat is sufficient to raise the temperature of a gram of the substance one degree. For many of the metals the specific heats were known with a fair degree of accuracy at the beginning of last century. Working further on the determination of these data two French physicists, Dulong and Petit, in 1810, made the interesting discovery that the observed specific heats seemed to vary inversely as the corresponding atomic weights as determined by Berzelius. For many of the metals the product of the atomic weight and the specific heat was found to be practically a constant. They found further, however, that to bring the product of the atomic weight and specific heat of sulphur as given by Berzelius in 1815 to agree with the products for the metals the atomic weights of many of the latter would have to be reduced to one half the figures then given. Because of this suggestion and for other reasons these atomic weights were actually reduced and so appear in the table of 1826.

In explanation of this interesting relation of atomic weights to specific heats Dulong and Petit put forth the suggestion that the *atoms* have all the same capacity for heat and that therefore the specific heat of a mass of any given substance would depend on the number of atoms in that mass and consequently on the atomic weights; of the heavy atoms a smaller number would suffice to make up a given weight than is the case with the light atoms. To illustrate this the following short table is appended, in which the atomic weights and specific heats as now everywhere accepted are employed. This will prove more satisfactory than to use the large numbers on the oxygen standard of Berzelius.

	Atomic Weight.	Specific Heat.	Product.
Antimony	120.2	0.0523	6.3
Copper	63.6	0.0930	5.9
Iron	56.0	0.112	6.3
Magnesium	24.4	0.245	6.0
Manganese	55.0	0.122	6.7
Mercury	200.0	0.0319	6.4
Platinum	194.8	0.0325	6.3
Silver	107.9	0.0560	6.0
Thallium	204.1	0.0335	6.8
Zinc	65.4	0.0932	6.1
Lead	206.9	0.0315	6.5
Uranium	238.5	0.0280	6.7
Gold	197.2	0.0324	6.4
Bromine	80.0	0.0843	6.7
Iodine	127.0	0.0541	6.8

It is observed that the product is nearly a constant, and this not far from 6.4. With the large numbers of Berzelius the product would be about 40.

If it may be assumed that this relation holds good for all substances, it will be recognized that we have a very simple method of arriving at atomic weights which cannot be fixed in any other manner. It is only necessary to divide the constant, 6.4, by the experimentally found specific heat to reach a number which must be very near to the real atomic weight. For instance, the specific heat of thallium is .0335. This divided into 6.4 gives 191, which is very near the atomic weight found by analysis. More will be said about this presently.

THE ELECTROLYTIC EQUIVALENTS OF FARADAY.

In 1834 Faraday made the discovery that when an electric current passes through an electrolyte the amount of substance separated at the electrodes depends only on the intensity of the current. If a number of electrolytes are placed in a series and a current passed through the whole, what may be termed *equivalent* amounts of the elements are separated in the same time. If we have in the circuit acidulated water, copper sulphate, silver nitrate, a zinc and an iron compound, it will be observed

that in the time required to liberate 1 gram of hydrogen from the water the following weights of the metals are separated:

Copper	31.6 grams.
Silver	107.1 grams.
Zinc	32.4 grams.
Iron	27.8 grams.

Such results were obtained for a large number of elements by Faraday and others, and the numerical values found were by many looked upon as representing the real atomic weights. But difficulties soon appeared when it was noticed that the amount of separated substance depends in some cases on the compound from which it is electrolyzed. While, for instance, 31.6 Gm. of copper separates from the sulphate, 63.2 would be liberated from certain other compounds. For a certain class of iron compounds the iron separated amounts to 27.8 Gm., but for another class it amounts to only 18.53 Gm. in the same time. It is not clear which one of these should be taken as the real atomic weight, or whether either should be taken. Other instances might be given in which the electrolytic equivalents vary with the nature of compounds from which obtained. It is apparent, therefore, that this method of fixing atomic weights needs itself a modification or correction.

By this time it is evident to the student that through the multiplication of methods proposed for fixing the atomic weights great confusion must have resulted. This was indeed the case, and the confusion extended to the formulas written to express the composition of many simple compounds. Water, for instance, was represented by four different formulas by as many different schools of chemists, and the reader was often at a loss to understand the structure of a body as expressed by symbols. This confusion existed until after the middle of the nineteenth century, and various suggestions were made to reconcile conflicting views through a more rational foundation hypothesis.

THE LAW OF AVOGADRO.

It was stated some pages back that Avogadro was among the first to recognize the value of the work of Gay Lussac and Humboldt on the combination of gases by volume. He was the first to draw a conclusion of the highest importance from them, which is now expressed by the law bearing his name, and which has become a foundation principle in modern scientific chemistry. The *Law of Avogadro* may be stated in this way: *Equal volumes of all gases under like conditions of temperature and pressure contain the same number of molecules.* The statement of the law includes the provision that the gas volumes compared must be taken at identical pressures and temperatures, inasmuch as changes in either would cause corresponding changes in the volumes, and therefore in the number of molecules in a given space.

This differs from the conception of Berzelius in one important particular. The latter assumed that the ultimate particles of the simple gases exist in the atomic condition, and that equal volumes contain the same number of these atoms. But, according to the view of Avogadro, these "integrant particles," or molecules may be and usually are made up by the union of several atoms. A liter of hydrogen, a liter of oxygen, a liter of carbonic acid gas and a liter of ammonia all contain the same number of molecules. It must be said here that the *proof* of this remarkable law belongs to the field of physics rather than to that of chemistry. Its truth was first recognized by physicists, especially in the development of the kinetic theory of gases, and was later accepted by chemists.

It follows directly from the law of Avogadro that molecular weights of simple or compound gases are proportional to their densities. In the following table the densities of a number of gases referred to hydrogen are given and in the last column the molecular weights of the same gases on the *assumption* that the density of the molecule of hydrogen referred to its atom is 2, or in other words that the molecule of hydrogen contains 2 atoms. The reason for this assumption will follow.

	Density.	Molecular Weight.
Hydrogen	1.00	2.0
Oxygen	16.00	32.0
Water vapor	9.00	18.0
Chlorine	35.50	71.0
Hydrochloric acid	18.25	36.5
Bromine	80.00	160.0
Hydrobromic acid	40.50	81.0
Sulphur (above 1000°)	32.10	64.2
Hydrogen sulphide	17.05	34.1
Nitrogen	14.00	28.0
Ammonia	8.50	17.0
Carbon monoxide	14.00	28.0
Carbon dioxide	22.00	44.0
Marsh gas	8.00	16.0

The following considerations indicate why it is believed that the molecules of hydrogen, chlorine, oxygen and certain other elements contain two atoms, or have a molecular weight equal to twice their atomic weights. It was shown some pages back in what proportions certain gases combine by volume. Accepting the hypothesis of Avogadro as correct, we may substitute for *volume proportions* molecular proportions, and thus reach this table:

1 molecule of hydrogen + 1 molecule of chlorine
= 2 molecules of hydrochloric acid.
2 molecules of hydrogen + 1 molecule of oxygen
= 2 molecules of water.
3 molecules of hydrogen + 1 molecule of nitrogen
= 2 molecules of ammonia.

Now, it appears that from the one molecule of chlorine we obtain chlorine enough to form two molecules of hydrochloric acid, each one of which must contain both chlorine and hydrogen. The chlorine molecule must, therefore, split into two portions to do this, and these two portions are its ultimate atoms. What is true of chlorine is also true of hydrogen. The oxygen for the two molecules of water vapor comes from the one molecule of oxygen, and the nitrogen for the two molecules of ammonia from the one molecule of nitrogen. It must follow, there-

fore, that the oxygen and nitrogen molecules are also double because they divide into two portions in going into combination. The following formulas express, then, what has just been said:

$$H_2 + Cl_2 = 2HCl$$
$$2H_2 + O_2 = 2H_2O$$
$$3H_2 + N_2 = 2H_3N$$

It would, in fact, be more accurate to say that the hydrogen, oxygen, chlorine and nitrogen molecules contain *at least* two atoms. Assuming these molecules to contain n atoms the following equation would also be true:

$$H_n + Cl_n = 2H_{\frac{1}{2}n}Cl_{\frac{1}{2}n}$$

We have here a splitting into two parts as before. But, granting the possibility of such a combination, we should expect to find in some gaseous hydrogen compound less than half as much hydrogen as we find in what we call the hydrogen molecule. However, no such compound has ever been discovered. We have several hydrogen compounds which contain in a given volume just half as much hydrogen as we find in the same volume of pure hydrogen gas, but no compound is known in which the ratio is below this. We are therefore justified in placing the molecular weight of hydrogen as 2 on the scale which has the atom of hydrogen as its basis, and from this the other molecular weights in the table above follow.

Suppose now that we apply these principles to the determination of the atomic weight of carbon. What we do practically is to find the smallest weight of carbon occurring in the molecular weight of any carbon compound which can be studied in the gaseous condition. A large number of such compounds are known and analysis shows that the smallest amount of carbon found in the molecular weight of any one of them is 12. Thus, marsh gas, with a molecular weight of 16, contains 4 parts of hydro-

gen and 12 parts of carbon. The molecular weight of carbon dioxide is 44 and we find here, by exact analysis, with 32 parts of oxygen 12 parts of carbon. The molecular weight of carbon monoxide is 28, and this we find is made up of 12 of carbon with 16 of oxygen. If, however, we should find a carbon compound with only 6 parts of carbon in the molecular weight, as derived from the gas density, we should be obliged to conclude that 12 represents the weight of *two* atoms. In reality, therefore, 12 is the maximum atomic weight which may be assigned to carbon. We are obliged to admit that it may be smaller, although the likelihood of this is very remote in view of the thorough study already given to carbon compounds. In the same manner, from their combining proportions with hydrogen and oxygen and from a determination of molecular weights of their compounds, the atomic weights of the other elements in the above table may be reached.

Fortunately, in the application of the law of Avogadro to the fixing of atomic and molecular weights we are not limited to the light elements. A few of the heavy metals may be vaporized under conditions which permit a weighing of the vapor, and for a still greater number of metals we are acquainted with compounds which are volatile. For zinc, cadmium and mercury the vapor densities have been determined with a fair degree of accuracy. The vapor densities of some of their compounds have also been found, so that the weight of the atom in the molecule may be determined. Volatile compounds of aluminum, iron, lead, thallium, tin, antimony, bismuth, chromium and several other metals have also been studied and from them atomic weights derived.

The credit of having presented the wide applications of the law of Avogadro in a clear and simple light belongs largely to the Italian chemist Cannizzaro, who in 1858 published a valuable paper on the subject. In this he pointed out also that the atomic weights derived from specific heat determinations agree with those found from vapor densities in a number of cases where both kinds of experiments could be made. Since his time many new observations have been made which confirm his views

fully. The important theoretical writings of Lothar Meyer contributed especially to clear up the subject.

Having now two methods which, when applicable, yield concordant results, it is possible to control the values reached through a third method, the observation of isomorphism, for a large number of cases. Thus, we find the atomic weight of zinc from its vapor density and specific heat. As isomorphous with zinc we have the metals in a well characterized series of sulphates. The amount of metal which replaces 65.4 parts of zinc in these sulphates we look upon as the atomic weights of these metals. For most of these metals we are not able to determine the atomic weights through vapor density, but specific heat determinations are possible, and the results obtained here are in perfect accord with those drawn from observations of isomorphous compounds.

Three general methods are therefore in practical use to fix atomic weights. These are:

1. From the molecular weights as found by the law of Avogadro.

2. From determination of specific heats of bodies in the solid condition.

3. From a determination of the weights of the substances which replace each other in isomorphous compounds.

Some illustrations will be given below.

DETERMINATION OF VALENCE.

In the sixth chapter the general notion of what is understood by valence was outlined, but nothing was said as to how it may be determined. In most instances a knowledge of the atomic weight of an atom is necessary to fix its valence. In certain gaseous compounds it follows almost directly from the manner of combination of their elements.

Fluorine, chlorine, bromine and iodine form only one combination with hydrogen, with which they unite, in the gaseous condition, volume for volume with no condensation. They must have, therefore, the same valence as hydrogen, which arbitrarily we assume to be unity, as

we have no knowledge of the real nature of this property of atoms. Oxygen, sulphur and a few other elements can combine with twice the volume; nitrogen, arsenic and phosphorus with three times the volume; and carbon and silicon with four times the volume that can be held by a chlorine atom. The following short table illustrates these types of combination:

HF	H_2O	H_3N	H_4C
HCl	H_2S	H_3P	H_4Si
HBr	H_2Se	H_3As	
HI	H_2Te		

The elements in the first column, combined with hydrogen, are called univalent; those in the second column are called bivalent; those in the third are called trivalent; those in the fourth quadrivalent.

Elements which are capable of replacing hydrogen, atom for atom, in the compounds of the first columns are, like hydrogen, univalent, and this is determined by the observation that in these compounds 1 part of hydrogen is replaced by weights of the elements represented by their atomic weights. Thus, we say that lithium, sodium, potassium and silver are univalent because 1 part of hydrogen may be replaced by 7, 23, 39.1 and 107.9 parts respectively of these metals; that is, by amounts corresponding to their atomic weights. The elements calcium, barium, strontium and magnesium are held to be bivalent, because amounts corresponding to their atomic weights replace *two* atoms of hydrogen from two molecules of the compounds in the first column, or two atoms of hydrogen in one molecule of the compounds in the second column above. Thus, 40.1 parts of calcium, or 1 atomic weight, combine with 71 parts, or 2 atomic weights of chlorine. The same weight of calcium combines with 16 parts, or 1 atomic weight of oxygen. In the same way aluminum is considered a trivalent element because 27.1 parts, representing 1 atomic weight, combine with 3×35.5 parts of chlorine. Also, 2×27.1 parts of aluminum combine with 3×16 parts of oxygen.

In general, therefore, the valence of an element may be fixed by a study of the compounds it forms with elements of known combining capacity, preferably with hydrogen, oxygen, chlorine or nitrogen. For many of the elements, it has been discovered, the combining capacity is not constant, which fact is illustrated in the table given in Chapter VI. As yet no satisfactory explanation has been offered to account for this, although there seems to be a relation here to the electric charges held by the atoms.

With the data at our command suppose we attempt to determine the atomic weight of some element, say thallium. This may be done by several methods, and among them by finding the amount of the metal in combination in pure thallium sulphate. We are supposed to know the composition of various sulphates. Lead sulphate is $PbSO_4$, which contains 206.9 parts of lead to 96.1 parts of SO_4, and this 206.9 represents the atomic weight of lead. Potassium sulphate is K_2SO_4, in which we have 78.2 parts of potassium to 96.1 parts of SO_4. This 78.2 is the weight of 2 atoms of potassium, as we discover from other investigations. Potassium must be a univalent element, while lead is bivalent. Now, when we examine thallium sulphate we find for 96.1 parts of SO_4 408.2 parts of thallium. If thallium is a bivalent element like lead this must be its atomic weight. If, on the other hand, it is univalent, like potassium and sodium, 408.2 must represent the weight of 2 atoms, giving for the atomic weight 204.1. In some respects the thallium compounds resemble those of lead very closely, and the metals themselves are much alike. In other respects thallium should be considered as allied to the alkali metals sodium and potassium. It dissolves in water at a high temperature, forming an alkaline hydroxide. The carbonate is also soluble and alkaline, while that of lead is insoluble. We have here, therefore, an illustration of a common dilemma which presents itself in the practical determination of atomic weights from combining proportions, and recourse must be had to an independent method to settle the question. Notwithstanding the resemblance of some

of the thallium salts to those of lead, the analogies with alkali metal compounds are closer and more characteristic. Thus, its sulphate is soluble and isomorphous with potassium sulphate. It replaces the latter in common alum, giving a thallium alum, isomorphous with potash alum. It forms several other compounds isomorphous with potassium compounds. From these facts it would appear that thallium should be taken as a univalent element, with the atomic weight 204.1.

The specific heat of thallium has been determined, first by one of the discoverers of the metal, Lamy, who found it to be 0.0325. Later, a more accurate determination made it 0.0335. From the law of Dulong and Petit we find the atomic weight by dividing this into the common atomic heat, 6.4. The quotient in this case is 191, which is a number sufficiently near 204.1 to fix this as the atomic weight rather than 408.2.

Few of the thallium compounds are volatile enough to admit of a molecular weight determination from vapor density according to the law of Avogadro, but one of the chlorides may be vaporized without decomposition. Roscoe determined the vapor density of thallous chloride and found it, referred to air, to be 8.2. This gives for the molecular weight, referred to hydrogen, 236.7, which is very close to the theoretical molecular weight 239.6, corresponding to TlCl. The atomic weight of thallium must, therefore, be taken as 204.1, making the atom univalent and the formula of the sulphate analyzed Tl_2SO_4, and not $TlSO_4$. These suggestions illustrate the usual procedure in determinations of atomic weight. It is first necessary to find by exact analysis or synthesis the combining value of the body in question with some element or group of known valence. Then it remains to fix, by one or all of the three methods given, this combining weight as the real atomic weight or as a multiple of it.

CHAPTER XIII.

CLASSIFICATION OF THE ELEMENTS.—GENERAL PROPERTIES OF THE METALS AND THEIR SALTS.

In the preceding chapters some of the most important elements with a few of their compounds have been described. The order in which the several elements were considered was a practical rather than a scientific one, being determined largely by their abundance and general usefulness in the arts in some cases, and in others by peculiarities in the classes of compounds formed with them. These elements are frequently spoken of as the *negative* or *non-metallic* elements. Most of them combine readily with the so-called *positive* or *metallic* elements, which remain to be described. Before taking up a discussion of the metals a systematic classification of the elements, as a whole, must be given and that will follow here.

From the very nature of the case it is evident that any classification attempted must be in many respects arbitrary. The common grouping of the elements as *metals* and *non-metals* is an illustration of an arbitrary division which, while useful in some directions, is very unsatisfactory in others, for the simple reason that there is no sharp line of demarcation between the two groups. Many substances can be considered just as well in one group as in the other. In the preceding pages the student has seen that certain elements were naturally thrown together. Thus fluorine, chlorine, bromine and iodine form a natural family and have been so considered by chemists for many years. Sulphur, selenium and tellurium are similarly treated because in their properties and in the compounds they form they show marked resemblances. Among the metals similar related substances will be

found. The following table shows several families or groups of triads to which attention was early called by different chemists.

The names of the elements and the corresponding atomic weights are given:

Lithium 7.03	Calcium..... 40.10	Sulphur 32.06
Sodium..... 23.05	Strontium..... 87.60	Selenium 79.20
Potassium 39.15	Barium 137.40	Tellurium.....127.60
Chlorine 35.45	Iron 55.90	Osmium.....191.00
Bromine 79.96	Nickel 58.70	Iridium 193.00
Iodine 126.97	Cobalt..... 59.00	Platinum 194.80

The properties of the elements in these groups vary with changes in the atomic weights. In the iron group the weights are nearly the same and we find that the metals and their compounds are much alike. The same is true in the platinum group. A consideration of such relations would seem to suggest that the properties of elements may depend on their atomic weights, and this has been shown to be in a marked degree the case.

THE PROPERTIES OF THE ELEMENTS AS PERIODIC FUNCTIONS OF THEIR ATOMIC WEIGHTS.

In order to show any relations existing between the atomic weights and properties of elements let us write their symbols in the order of increasing weights, beginning with lithium, as follows:

Li, 7.03; Gl, 9.1; B, 11.00; C, 12.00; N, 14.04; O, 16.00; F, 19.00.

We have here a gradual increase in the atomic weights and a well characterized change in properties corresponding. Lithium is strongly metallic and positive in its behavior, while fluorine is as certainly non-metallic and negative. The next greatest atomic weight is that of sodium = 23.05. But we have here an element with properties like those of lithium rather than like those of fluorine. Sodium evidently does not follow the latter ele-

ment in the series as begun. Let us therefore make a new series, parallel with the first, which runs thus:

Na, 23.05; Mg, 24.36; Al, 27.1; Si, 28.4; P, 31.0; S, 32.06; Cl, 35.45.

We have a new series of seven elements, beginning with a characteristic metal and ending with a characteristic non-metal. The corresponding elements in the two series resemble each other very closely in their chemical behavior and in the compounds they form. It appears from this that certain properties are repeated in passing through a series or period of seven elements, involving a change in atomic weight of about 16 units. What has been done here for fourteen elements may be done for many more. This grouping was suggested nearly 40 years ago by Lothar Meyer and D. Mendelejeff, independently, and is called the Periodic Arrangement of the elements. It is shown in the following table in which the symbols and atomic weights are given, and also the differences in atomic weights in passing from one period to another. Some of the elements cannot be well included in the seven families or groups as first indicated and are therefore placed in a separate or eighth group.

This periodic arrangement of the elements is often called the *natural* arrangement, but the appropriateness of this term may not be immediately apparent. The close relations of the elements of the first group, Li, Na, K, Rb and Cs and their compounds are easily recognized, but the position of the other elements, Cu, Ag and Au is not as evident. In studying the compounds of the metals later the student will find that the strongest likenesses are found between these compounds rather than between the metals themselves. In the next group the metals Gl, Mg, Ca, Sr and Ba are very closely related, while among their compounds there are the closest resemblances. The salts of Zn and Cd are in many instances much like those of Mg, and hence the propriety of grouping them all together. The evidence for the position of Hg is not as clear. In the third and fourth groups there are a number of rare elements which are not as easily compared; but in the fifth group N, P, As, Sb and Bi form

Periodic System of the Elements. O = 16.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Li 7.03	**Gl** 9.1	**B** 11.00	**C** 12.00	**N** 14.04	**O** 16.00	**F** 19.00	
Diff. 16.02	15.26	16.10	16.40	16.96	16.06	16.45	
Na 23.05	**Mg** 24.36	**Al** 27.10	**Si** 28.40	**P** 31.00	**S** 32.06	**Cl** 35.45	
Diff. 16.10	15.74	17.00	19.70	20.20	20.04	19.55	**Fe** 55.90
K 39.15	**Ca** 40.10	**Sc** 44.10	**Ti** 48.10	**V** 51.20	**Cr** 52 10	**Mn** 55.00	**Ni** 58.70
Diff. 24.45	25.30	25.90	24.40	23.80	27.10	24.96	**Co** 59.00
Cu 63.60	**Zn** 65.40	**Ga** 70.00	**Ge** 72.50	**As** 75.00	**Se** 79.20	**Br** 79.96	
Diff. 21.90	22.20	19.00	18.10	19.00	16.80		**Ru** 101.70
Rb 85.50	**Sr** 87.60	**Yt** 89.00	**Zr** 90.60	**Cb** 94.00	**Mo** 96.00		**Rh** 103.00
Diff. 22.43	24.80	26.00	28.40	26.20	31.60		**Pd** 106.50
Ag 107.93	**Cd** 112.40	**In** 115.00	**Sn** 119.00	**Sb** 120.20	**Te** 127.60	**I** 126.97	
Diff. 24.97	25.00	23.90	21.20	20.30	16.00		
Cs 132.90	**Ba** 137.40	**La** 138.90	**Ce** 140.20	**Pr** 140.5	**Nd** 143.6	**Sm** 150.3	
Diff.		34.10					**Os** 191.00
		Yb 173.00		**Ta** 183.00	**W** 184.00		**Ir** 193.00
Diff.		31.10		25.50			**Pt** 194.80
Au 197.20	**Hg** 200.00	**Tl** 204.10	**Pb** 206.90	**Bi** 208.50			
Diff.			25.60				
			Th 232.50		**U** 238.50		

a line as they should on account of the related compounds they yield with several other elements.

In the sixth group we have O, S, Se, Te, the relations of which have been already pointed out. Also, as a subgroup, Cr, Mo, W and U are naturally and closely related. In the seventh group the analogies of F, Cl, Br and I are well marked and already known to the student. The position of Mn may be questioned, as we think of this element as characteristically metallic. But, like chromium, we have here an element which often acts in the non-metallic condition forming salts known as manganates and permanganates, which latter resemble the perchlorates in some respects, and this in a measure justifies its position as a part of the group.

It will be noticed that a number of vacant spaces are left in the table. As first published spaces were left after Ca and Zn. Mendelejeff predicted the discovery of elements to fill these places and also, approximately, their atomic weights and physical properties. Later scandium, gallium and germanium were found in rare minerals and investigation showed that they would occupy the vacant spaces very well. Some of the spaces still empty may yet be filled by known elements after a more thorough study of their properties. A number of rare metals are known to which atomic weights between about 140 and 180 have been given. Further investigation is needed to settle fully the true weights of these substances and their properties.

Notwithstanding the evident shortcomings of the table, it presents as a whole the most consistent arrangement of the elements yet attempted and in the following chapters they will be studied in families or groups as shown. The student will then see relations more clearly than can be pointed out in this brief introduction.

ATOMIC VOLUMES.

Some interesting relationships are disclosed when we compare the relative volumes occupied by an atom of each of the metals. These relations may be best shown by comparing the volumes filled by atomic weights of the

different elements expressed in grams. The term atomic volume is applied to the quotient obtained by dividing the atomic weight in grams by the specific gravity of the element. Thus, for iron we have $\frac{5}{7}\frac{6}{8} = 7.2$. That is, the atomic weight of iron in grams occupies 7.2 cubic centimeters. Whether we use grams, milligrams or millionths of milligrams as our standard of weight, the relations between the atomic volumes calculated must remain the same. In the following chapters the numerical values of the atomic volumes will be given and their relations shown.

THE VALENCE OF THE GROUPS IN THE PERIODIC SYSTEM.

It has been pointed out that the maximum valence of most of the elements is shown by the number of the group to which they belong. There are a few exceptions to this statement, but the general truth of it is so striking that a table in illustration of the facts is here appended. The valence is measured by the oxygen combining power of the atoms, and for the purpose of better comparison the formulas in some of the groups are doubled, so as to have always two atoms of each element in combination with the oxygen. Thus, lime is written Ca_2O_2, instead of CaO, as usual.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Li_2O	Gl_2O_2	Ba_2O_3	C_2O_4	N_2O_5			
Na_2O	Mg_2O_2	Al_2O_3	Si_2O_4	P_2O_5	S_2O_6	Cl_2O_7	
K_2O	Ca_2O_2	Sc_2O_3	Ti_2O_4	V_2O_5	Cr_2O_6	Mn_2O_7	
Cu_2O	Zn_2O_2	Ga_2O_3	Ge_2O_4	As_2O_5	Se_2O_6	Br_2O_7	
Rb_2O	Sr_2O_2	Yt_2O_3	Zr_2O_4	Cb_2O_5	Mo_2O_6		Ru_2O_8
Ag_2O	Cd_2O_2	In_2O_3	Sn_2O_4	Sb_2O_5	Te_2O_6	I_2O_7	
Cs_2O	Ba_2O_2	La_2O_3	Ce_2O_4	Ta_2O_5	W_2O_6		Os_2O_8
Au_2O	Hg_2O_2	Tl_2O_3	Pb_2O_4	Bi_2O_5	U_2O_6		

Among the exceptions referred to these should be mentioned: bivalent compounds of copper are well known, and the oxide CuO is a common substance; some of the most stable compounds of gold are trivalent, instead of

univalent; in the eighth group the higher oxygen compounds are not well characterized, and are therefore omitted. Otherwise, the table shows highly instructive relations in condensed form and should be thoroughly studied.

THE METALLIC ELEMENTS.

As already intimated, the distinction between metallic and non-metallic elements is not a very sharp one, but is observed in a general way as a matter of convenience. The metallic characteristics of all the elements of the first and second groups in the periodic system are well defined and easily observed. At the beginning of the third group we find, however, an element which behaves in general as a non-metal. The other elements of the group show pronounced metallic properties. In the fourth group carbon and silicon are pronounced non-metals, while the others may be considered in general as metals. The first elements in the fifth and sixth groups are non-metals, while the others are more distinctly metallic. Arsenic illustrates well the difficulty in drawing a close distinction between the two classes of elements. In its physical appearance it is metallic, resembling cast iron; but on the other hand, in its most characteristic combinations it forms the non-metallic or acid part. In the seventh group all the elements, with the exception of manganese, are pronounced non-metals. In the eighth group all the elements are properly metals.

From a merely superficial point of view we distinguish certain properties which are spoken of as *metallic properties*. The most characteristic of these are *luster, high specific gravity, hardness, conducting power for heat and electricity, malleability, ductility, and capability of forming alloys*. But few of the metals possess all of these properties in a marked degree.

Alloys are combinations formed between metals, in which, as a rule, the combining proportions bear no relation to atomic weights. Thus, brass is an alloy of copper and zinc in the proportion 2:1, approximately, while the atomic weights are 63.6 and 65.4. An *amalgam* is an alloy in which one of the metals is mercury. Among the

common alloys there may be mentioned brass, solder, type metal, pewter, German silver, bronze and the mixtures employed in coinage and jewelry.

In alloys, as a rule, the melting point is below that which would be calculated from the proportions and melting points of the constituents taken. In some cases it is below that of the most readily melted of its constituents. Fusible metals and very soft solders are made of such mixtures, some of which will be described later.

IMPORTANT CLASSES OF METALLIC COMPOUNDS.

The student is already familiar with the fact that compounds are usually formed by combination of elements of opposite chemical nature. In Chapter IV it was shown that salts are formed by the union of metals with non-metals or by the action of metals on acids. Salts constitute a very important class of inorganic compounds. The oxides and hydroxides of the metals are also important and numerous.

The following brief definitions may be found useful to the student:

Acids are compounds formed by the union of hydrogen with non-metallic elements, or groups, the hydrogen being replaceable by metals to form salts. Acid oxides or anhydrides are combinations of oxygen with non-metallic elements, which unite with water to form acids. Thus, SO_2 unites with water to form H_2SO_3.

Bases are combinations of metallic elements with hydrogen and oxygen, united as hydroxyl. Thus, KOH and $Al(OH)_3$ are bases. The bases which are soluble in water are *alkalies*. KOH, NaOH and $Ba(OH)_2$ are illustrations. Basic oxides or anhydrides are combinations of metallic elements with oxygen; they yield bases by combination with water, and form salts by combination with acids or acid anhydrides. Thus, CaO is a basic oxide; with water it forms $Ca(OH)_2$, a true base. With SO_3 it forms $CaSO_4$.

Salts are compounds formed by the union of metallic with non-metallic elements. Practically they may be made by combination of the metal with the non-metal directly, as $Na + Cl = NaCl$; or by the action of an acid on the metal, as $Zn + H_2SO_4 = ZnSO_4 + H_2$; or by the union of an acid with a base, as $HCl + KOH = KCl + H_2O$; or by the union of a basic oxide with an acid oxide, as $K_2O + SO_3 = K_2SO_4$. Salts are formed also by a variety of indirect methods, but these illustrations sufficiently characterize their composition.

According to the ionic hypothesis all these bodies undergo a breaking up or *dissociation* when dissolved in water. But it has recently been observed that an analogous dissociation must follow in many non-aqueous liquids also.

The following list embraces the most important classes of metallic compounds, some of which will be but briefly considered in discussing the metals:

1. Oxides and hydroxides.
2. Sulphides.
3. Carbonates.
4. Halogen salts, or binary compounds of fluorine, chlorine, bromine and iodine.
5. Compounds with the acids of sulphur; sulphites and sulphates.
6. Compounds with the acids of nitrogen; nitrites and nitrates.
7. Compounds with the oxygen acids of the halogens; hypochlorites, chlorates, etc.
8. Borates, phosphates, arsenites, arsenates, chromates, manganates and silicates.

Generalities on these Compounds.

Oxides. The important groups of oxides are illustrated in the short table above in which variations in valence are shown. The oxides of lithium, sodium, potassium, rubidium and cæsium dissolve readily in water forming alkaline hydroxides. The oxides of calcium, strontium and barium dissolve slowly, forming alkaline

hydroxides. One of the oxides of thallium, Tl_2O, dissolves easily, forming a hydroxide like those of sodium and potassium. The highest oxides of chromium and manganese dissolve in water, forming acids. Practically all of the other oxides of the metals are insoluble in water.

Hydroxides. The method of forming some of the hydroxides has just been explained. Those insoluble in water are mostly formed by precipitating a metallic salt by a soluble hydroxide, thus:

$$ZnSO_4 + 2KOH = K_2SO_4 + ZnO_2H_2$$

Some of these hydroxides redissolve in an excess of the precipitant. In presence of strong alkalies they appear to behave as acids. Thus zinc hydroxide forms potassium zincate:

$$ZnO_2H_2 + 2KOH = K_2O_2Zn + 2H_2O$$

The soluble hydroxides are alkalies; that is, they exhibit the reactions due to the presence of OH ions. These reactions are absent in the insoluble hydroxides, but the latter still have the property of neutralizing acids.

Sulphides. In many respects the sulphides resemble the oxides. Only those of the light metals are soluble in water. Many of them may be formed by the direct union of the metal with sulphur by the aid of heat. The sulphides of the heavy metals are mostly made by precipitation of their solutions by hydrogen sulphide or ammonium sulphide. Thus,

$$CuSO_4 + H_2S = CuS + H_2SO_4$$
$$ZnSO_4 + (NH_4)_2S = ZnS + (NH_4)_2SO_4$$

The behavior of the sulphides of most of the metals toward acids is characteristic and important in analytical chemistry, as illustrated in a preceding chapter. Many of the sulphides dissolve in acids, liberating hydrogen sulphide just as the corresponding oxides liberate water:

$$ZnS + 2HCl = ZnCl_2 + H_2S$$
$$ZnO + 2HCl = ZnCl_2 + H_2O$$

Several of the heavier sulphides dissolve in solutions of the alkali sulphides, forming a peculiar class of salts in which sulphur takes the place of oxygen. Thus,

$$K_2S + SnS_2 = K_2SnS_3,$$

which is called potassium thiostannate. This behavior is important in analytical chemistry, and is employed in the separation of metals.

Carbonates. The carbonates of the alkali metals are soluble in water. The others, with few exceptions, are insoluble. All carbonates are more or less readily decomposed by mineral acids. Two general classes of carbonates are distinguished, normal and acid, or bicarbonates. As illustrating the first kind, we have common sodium carbonate, Na_2CO_3. As illustrating the second, we have the acid carbonate, commonly called bicarbonate, $HNaCO_3$. Bicarbonates are usually made by the action of carbonic acid on carbonates. At a sufficiently high temperature carbonates decompose, with formation of carbon dioxide and a metallic oxide. As further illustrating the parallelism between oxygen and sulphur, it may be mentioned that we have a class of bodies called sulphocarbonates, or thiocarbonates, which may be formed by reactions analogous to those which yield carbonates:

$$K_2S + CS_2 = K_2CS_3$$
$$K_2O + CO_2 = K_2CO_3$$

Acids form with the first H_2CS_3, which breaks down into H_2S and CS_2. The second yields H_2O and CO_2 almost directly.

The soluble carbonates possess a strong alkaline reaction with the ordinary indicators and this is probably due to a decomposition in presence of water, in which a small part of the carbonate is changed in this way, the reaction being one of *hydrolysis,* as already referred to:

$$Na_2CO_3 + H_2O = HNaCO_3 + NaOH$$

The bicarbonate is neutral to our delicate indicators; its degree of dissociation is slight.

Halides. This term may be applied to the binary compounds of the metals with fluorine, chlorine, bromine and iodine. Of the formation and properties of the fluorides little need be said, as, with few exceptions, they are unimportant substances. The halogen compounds of most of the metals are soluble in water. Of the insoluble compounds those of silver, lead and mercury are the most characteristic. The halides may be formed by a number of general reactions, of which the following are the most important:

1. By direct union of metals with the halogen element, as:

$$Fe + Br_2 = FeBr_2$$

2. By action of a metal on a halogen acid, as:

$$Zn + 2HCl = ZnCl_2 + H_2$$

3. By the action of an oxide or hydroxide on a halogen acid, as:

$$K_2O + 2HCl = 2KCl + H_2O$$
$$KOH + HCl = KCl + H_2O$$

The halides of most of the metals are readily decomposed by strong sulphuric acid, with formation of a sulphate. From a fluoride, hydrofluoric acid is produced, and from a chloride, hydrochloric acid; but from bromides and iodides some free bromine and iodine are obtained.

Many of the halides are volatile at a high temperature without decomposition. From this behavior it has been found possible to determine their vapor densities and therefore molecular weights. In the halides the non-metallic element always acts with unit valence.

The solutions of the alkali halides are said to *dissociate* readily and are neutral. But halides of many of the heavy metals show an *acid* reaction in solution. This is appar-

ently due to hydrolysis, in which acid is liberated and exhibits the characteristic reaction, and in which a *non*-dissociated base is formed. Here the alkali reaction is lacking. With $FeCl_3$ we have, *to a slight extent,* this behavior:

$$FeCl_3 + 3H_2O = 3\overset{+}{H}, \overset{-}{Cl} + FeO_3H_3$$

The trace of acid is enough to show a reaction.

Sulphates, Sulphites and Allied Salts. It has been already pointed out that sulphur forms a number of oxygen acids. But the compounds of some of these are of little importance and need not be considered here. The sulphites, sulphates and thiosulphates will be briefly described.

As sulphurous acid, H_2SO_3, is a compound with both hydrogens replaceable we have two classes of salts from it, known as normal, and acid sulphites or bisulphites. These have the general formulas M_2SO_3 and $MHSO_3$. They are characterized by their instability in presence of oxidizing agents from which they take oxygen and become sulphates. On account of this behavior both classes of salts are used in photography as constituents of developers. The sulphites and acid sulphites are readily decomposed by acids with separation of SO_2, or formation of H_2SO_3 in weak solution. The normal and acid sulphites of the alkali metals are soluble in water; the normal sulphites of most of the other metals are either insoluble or but slightly soluble. The acid sulphites, however, are mostly soluble. Their solutions, like those of the acid carbonates, decompose on heating with separation of normal sulphite and escape of SO_2.

Sulphates are among the most important and abundant of inorganic salts. They are most readily formed by solution of metals, oxides or carbonates in dilute sulphuric acid. Acid sulphates of the type $MHSO_4$ are known, but with the exception of the sodium and potassium compounds they have little importance. Most of the normal sulphates are soluble in water and dilute acids. The sulphates of strontium and barium are practically

insoluble in water and dilute acids. Calcium sulphate is but slightly soluble in water. Lead sulphate is likewise but little soluble in water. This behavior is applied in analytical chemistry in the separation of sulphuric acid and also of the metals lead, strontium and barium.

Solutions of the sulphates of the light metals are neutral, but with the heavy metals we have usually a marked acid reaction for the reason just pointed out for the halide salts. On the other hand it has been shown that solutions of the alkali sulphites are alkaline, since hydrolysis here gives rise to a strong dissociated base and a weak acid.

At a certain temperature acid sulphates of the type $MHSO_4$ decompose, yielding pyrosulphates and water:

$$2MHSO_4 = M_2S_2O_7 + H_2O$$

At a higher temperature the pyrosulphate breaks up into normal sulphate and SO_3:

$$M_2S_2O_7 = M_2SO_4 + SO_3$$

Attention must be called to the nomenclature of these salts. Compounds of the type M_2SO_4 should be called sulphates or normal sulphates; those of the type $MHSO_4$ should be called acid sulphates, but are sometimes called bisulphates, which leads to confusion with the next group; compounds of the type $M_2S_2O_7$ should be called disulphates or pyrosulphates.

Of the pyrosulphates only those of sodium and potassium have technical importance.

A few thiosulphates are practically important. These are compounds of the type $M_2S_2O_3$ and may be looked upon as sulphates in which one atom of oxygen is replaced by S.

The thiosulphates of the alkali metals are the best known. The sodium compound is made in large quantities as described in a former chapter, and is used in photography. The thiosulphates are decomposed by dilute acids with precipitation of sulphur, and liberation of sulphurous oxide.

Nitrites. These salts are not numerous; only those of the alkali metals have importance. Nitrites are made by the action of nitrous acid on hydroxides,

$$HNO_2 + KOH = KNO_2 + H_2O,$$

or by the reduction of nitrates. When an alkali nitrate is heated to a high temperature it loses part of its oxygen. If heated with lead or copper it loses it very readily.

$$KNO_3 = KNO_2 + O$$

Most of the nitrites are very soluble in water.

Nitrates. These are very common and important salts and are best made by the action of nitric acid on metals, their oxides, hydroxides or carbonates.

All true nitrates are soluble in water. A few bodies known as basic nitrates are insoluble. All nitrates are decomposed when heated with sulphuric acid, and all suffer decomposition by heat alone. Some yield nitrites, as explained above. Some break down, yielding a metallic oxide, oxygen and nitric oxide, as shown by the behavior of lead nitrate referred to in chapter VI. All nitrates act as strong oxidizing agents when fused or strongly heated with many organic substances.

The Oxygen Salts of the Halogens. The nomenclature and general formulas of these bodies have been illustrated already. The acids may be represented by the formulas in the first column and the salts by the formulas of the second.

HOX	MOX
$HOXO$	$MOXO$
$HOXO_2$	$MOXO_2$
$HOXO_3$	$MOXO_3$

Salts of the four chlorine oxygen acids are known. Hypobromites and bromates are also known, while for iodine the iodates and periodates are the only stable compounds. The chlorine salts are all soluble in water;

the hypobromites are readily soluble, while the bromates are much less soluble; the iodates of the alkali metals are sparingly soluble in water. Most of the other iodates are insoluble.

The salts of all of these acids are decomposed by heat, a simple halide usually resulting. In some cases the decomposition takes place in two stages, as illustrated by the familiar reaction with potassium chlorate:

$$2KClO_3 = KClO_4 + KCl + O_2$$
$$KClO_4 = KCl + 2O_2$$

Sulphuric acid decomposes all the salts with liberation of acids and oxides. Under various conditions the salts are all oxidizing agents; some of them even give up their oxygen in simple aqueous solution to bodies easily oxidized. This is well illustrated by the action of sodium hypobromite on urea:

$$3NaOBr + CON_2H_4 = 3NaBr + CO_2 + 2H_2O + N_2$$

Several of the chlorates and hypochlorites are technically important; the alkali hypobromites are sometimes used as reagents, as illustrated by the above equation, while the other salts have little practical value.

Borates. As explained in the ninth chapter, boric acid forms a number of complex borates, which is possible from the peculiar composition of the acid. Three classes of borates are known: the orthoborates, M_3BO_3, which are not very stable, the metaborates, MBO_2, of which a number are well known, and the pyroborates, $M_2B_4O_7$, of which common borax is the best illustration. The alkali borates are soluble in water, the others are mostly insoluble. All borates are decomposed by strong sulphuric acid, with liberation of boric acid. The alkali borates may be made by direct union of boric acid with carbonates or hydroxides; the other borates are usually produced by precipitation.

The reason for the alkaline reaction of borax has been given already.

Phosphates. Three principal groups of phosphates, called metaphosphates, orthophosphates and pyrophosphates are known. The first are of the type MPO_3, the molecule of metaphosphoric acid resembling that of nitric acid. Metaphosphates seem to exist in condensed or polymeric types in which several molecules are united, as, $M_2P_2O_6$, $M_3P_3O_9$, $M_6P_6O_{18}$. The salts of the alkali metals only are well known; some are soluble in water, others not; all may be made from primary orthophosphates by heating and cooling carefully under varying conditions. By boiling solutions of metaphosphates orthophosphates are formed.

The orthophosphates, or common phosphates, are represented by the formulas M_3PO_4, M_2HPO_4 and MH_2PO_4, as phosphoric acid is tribasic. The nomenclature of these salts may be illustrated by the sodium compounds:

Na_3PO_4 is called normal sodium phosphate, trisodium phosphate or tertiary sodium phosphate.

Na_2HPO_4 is called disodium hydrogen phosphate or secondary sodium phosphate.

NaH_2PO_4 is called dihydrogen sodium phosphate or primary sodium phosphate.

The primary phosphates are soluble in water; the secondary and tertiary phosphates are mostly insoluble, those of the alkali metals being exceptions. The tertiary phosphates are very stable and withstand a high temperature. The secondary phosphates are converted into pyrophosphates by heat and the primary phosphates into metaphosphates. The soluble tertiary phosphates are strongly alkaline, the secondary phosphates feebly alkaline, while the primary phosphates are neutral or feebly acid with most indicators.

This behavior depends on the hydrolytic dissociation of the salts. The tertiary phosphate suffers some decomposition according to the scheme:

$$Na_3PO_4 + H_2O = HNa_2PO_4 + \dot{N}a, \bar{O}H$$

The secondary phosphate in turn appears to hydrolyze slightly in this way, to give a faint alkaline reaction:

$$HNa_2PO_4 + H_2O = H_2NaPO_4 + \dot{N}a, \bar{O}H$$

It must not be understood that any large fractions of the salts are dissociated in this way.

Pyrophosphates, as indicated by the name, are commonly made by heating orthophosphates. The pyrophosphates exist in two general classes, represented by the formulas $M_4P_2O_7$ and $M_2H_2P_2O_7$. The secondary orthophosphates, strongly heated, give the first, as

$$2HNa_2PO_4 - H_2O = Na_4P_2O_7$$

Primary phosphates moderately heated give the second class, as

$$2H_2NaPO_4 - H_2O = Na_2H_2P_2O_7$$

The alkali pyrophosphates are soluble in water, the others not. Solutions of pyrophosphates when heated with acids yield orthophosphates.

A few phosphites and hypophosphites are known, but as they are comparatively unimportant, they need not be discussed here.

Arsenites. These salts have the general formula M_3AsO_3. Those of the alkali metals may be prepared by dissolving arsenous oxide in solutions of hydroxides or carbonates. These products are soluble in water. The arsenites of the heavy metals are insoluble and are usually made by precipitation of the sodium or potassium salt by a salt of a heavy metal. Several metarsenites are known with the general formula $MAsO_2$.

Arsenates. Compounds of the general formula M_3AsO_4 are made by dissolving arsenic oxide in alkali solutions. Crude products are formed also by fusing a mixture of arsenous oxide, niter and alkali. The arsenates are isomorphous with the phosphates and resemble them in many respects. The normal arsenates of the alkali metals are soluble in water, the other arsenates are insoluble. Acid arsenates corresponding to acid phosphates are known. These have the general formulas MH_2AsO_4 and M_2HAsO_4. Hydrogen sulphide reduces acidified solutions of arsenates slowly, separating sulphur and precipitating As_2S_3.

Chromates. The salts of chromic acid have the formula M_2CrO_4, corresponding to the sulphates. The chromates of the alkali metals are soluble and are usually made directly from the common ore known as chrome ironstone, by fusion with alkali carbonate in presence of air. The chromates of the other metals are insoluble in water and are made by precipitation, as,

$$K_2CrO_4 + PbN_2O_6 = PbCrO_4 + 2KNO_3$$

By the action of acids chromates are converted into dichromates, or anhydrochromates, of the type $M_2Cr_2O_7$, thus:

$$2K_2CrO_4 + 2HCl = K_2Cr_2O_7 + 2KCl + H_2O$$

The dichromates are usually red, while the chromates are mostly yellow. The dichromates are active oxidizing agents, those of sodium and potassium being valuable mainly on this account. In presence of sulphuric acid and reducing bodies they give up oxygen in this way:

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

It will be recalled that the dichromate was employed in the liberation of chlorine from hydrochloric acid. This is also an oxidation reaction:

$$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

In both cases the acid combinations are destroyed and salts of chromium result.

Manganates. By fusion of powdered black oxide of manganese with caustic alkali in presence of oxidizing agents, or the air even, a green manganate results, M_2MnO_4. Such salts are not stable and are not important. By action of acids the manganates become converted into the permanganates, of which the potassium compound is the best known. It has the formula $KMnO_4$.

These salts are important because of the fact that they give up oxygen readily, and are extremely active oxidizing agents. Like the dichromates, they become reduced to salts of the active element in the decomposition:

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

The permanganates are all highly colored compounds, the common soluble salts being deep purple.

Silicates. In Chapter IX some of the important properties of silicic acid were explained and formulas of silicates given. Very few of the silicates can be made in pure condition and our knowledge is chiefly confined to mixtures obtained by fusion of silica with metallic oxides or carbonates, or to crude precipitation products formed by adding salt solutions to solutions of water glass. The silicates and borates are alike in this respect, that they exist in very complex condensed types which may be looked upon as derived from acids formed by the loss of one or more molecules of water from several molecules of ortho acid. Common borax is the sodium salt of the acid related to the ortho acid in this manner:

$$4H_3BO_3 - 5H_2O = H_2B_4O_7$$

Many silicates are similarly derived.

The salts of orthosilicic acid are called orthosilicates. Those from the first derived acid are called metasilicates. Salts derived from condensed silicic acids are called di-, tri-, or polysilicates in general. The following formulas illustrate this:

Orthosilicates	M_4SiO_4
Metasilicates	M_2SiO_3
Disilicates	$M_6Si_2O_7$
	$M_2Si_2O_5$
Trisilicates	$M_4Si_3O_8$
	$M_{10}Si_3O_{11}$

Solution Theories. In a former chapter a brief discussion of the ionic dissociation theory was given, and its applications in

explaining many chemical reactions pointed out. The bodies concerned here are the acids, bases and salts as above described and the theory of free ions aims to account for many phenomena observed when these compounds pass into solution. In going into aqueous solution these bodies, among other changes produced,

Lower the freezing point,
Elevate the boiling point,
Impart electrical conductivity.

In working with dilute solutions the effect does not decrease exactly in proportion to the amount of substance dissolved; in fact in very dilute solutions the molecules seem to become relatively *more active* in producing these effects, and behave as if they were split up into smaller groups or *ions*, each one of which has the activity of the original large group, as far as the freezing and boiling points, at any rate, are concerned. In respect to electrical conductivity it is held that the ions alone are able to conduct the current, and a solution which is a non-conductor, a pure sugar solution for example, is believed to hold no free ions. A five per cent solution of common salt is a relatively good conductor of electricity, but solutions of ten, fifteen or twenty per cent strength are not twice, three times or four times as good. It is held in such cases that as the concentration increases the ionization decreases, and in consequence the relative conductivity also.

But some of the properties of solutions are not so readily explained by the assumption of free ions, and several attempts have been made to provide a theory which will take into account more satisfactorily the behavior of the solvent, as well as the behavior of the substance dissolved. In the ion theory the water or other solvent is treated as an *inert* body which merely brings about dissociation without in any way combining with the dissociated particles. But many phenomena suggest that a solution is much more than a mechanical mixture of water particles and salt particles, for example; water itself is certainly a complex or *associated* substance in the ordinary liquid condition, and when bodies dissolve in it their molecules may enter into some sort of combination with one or more molecules of the water. On concentration or dilution the form of this combination must gradually change, until, in very dilute solutions, a condition of constancy is reached. The power of depressing the freezing point or elevating the boiling point of the solvent, or the power of conducting the electric current must vary with the complexity of these "hydrate" aggregations.

The so-called hydrate theory of solutions has not been developed as yet into a tangible system, as is the case with the ionic dissociation theory, but much may be expected of it when completely worked out.

SPECIFIC HEATS OF COMPOUNDS.

For a number of compounds it has been shown that the molecular heat is practically the sum of the atomic heats. To illustrate this it will be recalled that the following atomic heats are known and given in the last chapter: Lead, 6.5; silver, 6.0; bromine, 6.7; iodine, 6.8. From these numbers the molecular heats may be calculated as follows:

PbI_2,	$6.5 + 2 \times 6.8 = 20.1$.	$3 \times 6.4 = 19.2$
$PbBr_2$,	$6.5 + 2 \times 6.7 = 19.9$.	$3 \times 6.4 = 19.2$
AgI,	$6.0 + 6.8 = 12.8$.	$2 \times 6.4 = 12.8$
AgBr,	$6.0 + 6.7 = 12.7$.	$2 \times 6.4 = 12.8$

By actual experiment the specific heat of lead iodide has been found to be 0.0427, and that of lead bromide 0.0533. These numbers, multiplied by the corresponding molecular weights, give 19.7 and 19.6. respectively as the molecular heats. For silver bromide the specific heat of 0.074 has been found. This, multiplied by the molecular weight, gives 13.9, which is but little larger than the calculated number above. For silver iodide the observed value of the specific heat is 0.055, which gives a molecular heat of 12.9, very close to the calculated value. From such observations it has been found possible to make predictions concerning the numerical values of specific heats in advance of their actual determination.

Determination of Specific Heat. While this is a subject which properly belongs to physics, a brief explanation of the simple principle involved in practical methods may not be out of place. Knowing that the latent heat of the melting of ice is 79.5 units we can find the specific heat of many substances which are insoluble in water and do not decompose water, by observing how many grams of ice are melted by the cooling down of a given number of grams of the substance in question through a given range of temperature. To make this test the metal or other body under experimentation is warmed to a known temperature, say 100° C., and then

is brought immediately in contact with an excess of pure ice under such conditions that all its heat must be given out to melt part of it. This may be done by the aid of an apparatus called an ice calorimeter, shown in the next figure. This consists of a perforated receptacle, A, which is surrounded by the ice to be melted and covered by a

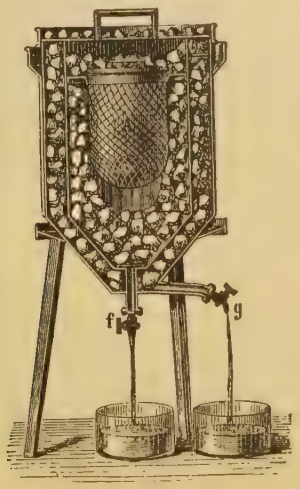

FIG. 26.

movable lid. This receptacle and the ice chamber around it are drained by the faucet f. Outside of this ice chamber is a second one drained by the faucet g, the object of which is to protect the inner ice chamber from atmospheric heat. Both chambers are covered by a lid holding ice.

Suppose now that we wish to find the specific heat of iron and that we take for experiment a ball of the pure metal weighing 250 Gm. We bring this to a temperature of 100° C., exactly, and then, without giving it an opportunity to cool in the air, drop it immediately into the vessel A, and replace the lid. The ice around A has the temperature 0°. Some of it melts, and the water formed

is after a time drawn off through f, and weighed or measured. Assume that the water collected weighs 38 grams. This is necessarily produced by the melting of 38 grams of ice; but to melt one gram of ice requires the addition of 79.5 units of heat. Therefore,

$$79.5 \times 38 = 3021 \text{ units}$$

are given to melt the 38 grams of ice. These units are furnished by the cooling of 250 grams of iron through 100°, because the end temperature of the metal must be 0°, with a great excess of ice in the apparatus. It follows, therefore, that one gram of iron in cooling down one degree must give out an amount of heat found by this division:

$$\frac{3021}{250 \times 100} = 0.12 \text{ unit.}$$

That is, each gram of iron gives out 0.12 unit of heat in cooling one degree C. To warm one gram of iron one degree would require the addition of the same amount of heat, and this, by definition, is the specific heat.

The method here briefly described was suggested by Black and improved by Lavoisier and Laplace, who introduced the form of calorimeter figured. The greatest accuracy is not possible with this apparatus, and besides relatively large weights of substance are required in the experiment, but it serves well to demonstrate the principle. Bunsen later constructed an ice calorimeter, which is used in very exact investigations with even small amounts of substance. In this apparatus the amount of melted ice is determined by the decrease of volume which follows when it is converted into water.

In another general method what is known as a water calorimeter is used. In this the elevation of temperature in a given weight of water is measured, when to it a given weight of the substance at a given temperature is added. Let a represent the weight of water in the calorimeter, b the weight of substance added to it, t' the original temperature of the water, t'' the temperature after mixing,

t''' the temperature of the substance before adding it to the water, then the specific heat, x, of the substance is given by the formula:

$$x = \frac{a(t'' - t')}{b(t''' - t'')}$$

This simple equation does not include a correction which in practice must be made for the amount of heat absorbed by the calorimeter itself. Other general methods employed in specific heat determinations are essentially modifications of the above.

CHAPTER XIV.

THE ALKALI METALS: LITHIUM, SODIUM, POTASSIUM, RUBIDIUM AND CÆSIUM. AMMONIUM COMPOUNDS.

GENERAL CHARACTERISTICS.

These metals form a natural group or family as already shown, and the resemblances extend through most of the compounds. The salts of ammonium are very similar to the alkali metal salts in many respects and therefore may be conveniently and properly described with them. The physical properties of the metals are shown in the following table:

	Atomic Weight.	Specific Gravity.	Atomic Volume.	Melting Point.	Boiling Point.
Lithium	7.03	.59	11.9	180°	
Sodium	23.05	.97	23.7	97	749°
Potassium	39.15	.87	44.8	62	720
Rubidium	85.45	1.52	56.2	38.5	
Cæsium	132.90	1.88	70.6	26.5	

The metals resemble each other closely in their behavior toward oxygen and water. They become coated with a film of oxide in dry air, and when heated burn readily. In water they dissolve, forming strongly alkaline hydroxides. Very few of the salts formed by these metals are insoluble in water, and these few are not important. The carbonate and phosphate of lithium are but slightly soluble and in this respect bear some resemblance to the corresponding magnesium compounds.

LITHIUM.

Occurrence. Very widely distributed in nature, being found in traces in all mineral waters, as chloride, car-

bonate or sulphate. It is found in several minerals, in many vegetable substances and has been detected in the blood. Yet it must be considered as one of the rare metals.

History. The metal was discovered in 1817 by Arfvedson, was isolated by Davy, and first obtained in pure form by Bunsen and Matthiessen in 1855 by electrolysis of the fused chloride.

Preparation. The metal is still isolated by the process last given.

Uses. The metal has no practical uses.

Salts of Lithium. Many compounds of the metal are known, but they are not abundant enough to be important. Lithium chloride is extremely soluble in water. Lithium phosphate requires about 2,500 parts of water for its solution. Lithium carbonate has some uses in medicine directly and in the preparation of several medicinal salts. But these applications seem to be based on erroneous notions and are not justifiable by scientific facts. Compounds of lithium are best recognized by the color they impart to the Bunsen flame and by the characteristic red line in its spectrum.

SODIUM.

Occurrence. This is one of the most widely distributed of the elements. It is found in largest quantity as the chloride in rock salt, sea salt and in many mineral springs; as nitrate in Chili saltpeter; as sulphate and carbonate in large deposits in several parts of the world and in many other compounds.

History. The metal was first isolated by Davy in 1807 by electrolysis of fused soda. It was later made by heating iron with caustic soda; and in greater quantity by heating a mixture of sodium carbonate and charcoal.

Manufacture. Until recently sodium has been used in large quantities for the production of aluminum, and this employment greatly stimulated the industry. Sod-

ium has usually been produced on the large scale by the reduction of the carbonate or hydroxide by some form of carbon, but the general process has undergone several modifications. By one method a mixture is made of 8 parts of dry sodium carbonate, 3 parts of powdered coal or charcoal and 1 part of chalk. This is mixed to a stiff paste with oil or tar, charged into an iron retort, and distilled. The iron retort is connected by a pipe with an iron box which is kept cold outside the furnace. By the decomposition of the chalk CO_2 is liberated, which helps to carry along the sodium vapors. These condense in the iron box which is emptied at the end of the distillation, the sodium being poured into petroleum. The reaction illustrating the reduction is this:

$$Na_2CO_3 + 2C = Na_2 + 3CO$$

In another process the reducing agent is a crude iron carbide obtained by heating a mixture of finely divided iron and tar and coking the same away from the air. This yields a body of the formula FeC_2. This carbide is mixed with caustic soda in the proportion of 10 parts of the latter to 7.5 of the former, and the mixture is distilled as before in a retort. The reaction takes place at a relatively low temperature and according to the equation:

$$3NaOH + FeC_2 = 3Na + Fe + 3H + CO + CO_2$$

The escaping gases assist in carrying the sodium vapor from the retort.

Two electrolytic processes are also in use for the separation of sodium and these are now more commonly followed than the above. In one the hydroxide, in molten condition, is decomposed at a temperature but little above its fusing point, which permits the easy removal of the liberated metal. In another process the chloride is mixed with potassium or calcium chloride, fused at a low red heat, and subjected to electrolysis.

Properties. The specific gravity, melting and boiling points of sodium have been given above. The metal is

silver white but tarnishes readily in the air. It decomposes water and other hydroxyl compounds readily with liberation of hydrogen. It is an interesting fact that with dry chlorine gas or pure liquid chlorine or bromine it is practically inert. In dry hydrochloric acid gas it remains unattacked for weeks. It will be seen in what follows that the same behavior is observed with other metals.

Uses. Sodium has been employed for the production of aluminum by the decomposition of the chloride at a high temperature:

$$AlCl_3 + 3Na = Al + 3NaCl$$

This process has been practically displaced by the cheaper electrolytic method. The separation of magnesium from the chloride is accomplished in the same manner:

$$MgCl_2 + 2Na = Mg + 2NaCl$$

It is employed in the production of sodium amalgam which is used for several purposes, also in making pure sodium hydroxide for some laboratory purposes and in various other ways.

Sodium Oxides. Several of these bodies have been described and one of them has recently become important. A mixture of Na_2O and Na_2O_2 is formed by burning sodium in dry air or oxygen. The oxide Na_2O_2, known in commerce as the dioxide, peroxide or superoxide, is made by passing pure dry air, CO_2-free, over metallic sodium heated in an iron pipe placed in a furnace. The sodium burns slowly and a white mass results. This is used in analytical chemistry and technology as an oxidizing agent, being valuable because of the readiness with which it gives up oxygen.

Sodium Hydroxide. This important compound is known as caustic soda and is made in enormous quantities for use in several industries. It is usually prepared

from the carbonate by boiling a solution of the latter with slaked lime:

$$Na_2CO_3 + CaO_2H_2 = 2NaOH + CaCO_3$$

On a smaller scale it is made by action of water on the metal:

$$Na + H_2O = NaOH + H$$

The following experiment illustrates this:

Experiment 154. Cut a gram or more of sodium into small bits, which throw into a beaker containing about 100 Cc. of water, one at a time, waiting until the action ceases in each case before adding another piece. Cover the beaker with a glass plate during the reaction. When this is complete, remove the glass and evaporate the solution to dryness, beginning in the beaker and finishing in a small porcelain dish. Observe the color of the solid substance obtained, and its action on the skin. Now add about 50 Cc. of water to the solid to dissolve it. Divide the solution into four portions. To one add a few drops of solution of phenol-phthalein in alcohol; to the second some solution of litmus, to which a drop or two of acid had been added; to the third some aqueous solution of methyl orange to which a trace of acid had been added; and to the fourth some solution of cochineal in weak alcohol, made acid with a few drops of hydrochloric acid. Observe the color of these solutions before they are added to the sodium hydroxide.

In each case a marked change in shade follows the mixing. The litmus, phenol-phthalein, methyl orange and cochineal are *organic* substances, which have one color in acid solutions and another in alkaline solutions. We have already had illustrations of this behavior, and we shall find others later. Our sodium hydroxide is one of the most characteristic of alkaline substances, and the colors produced above are essentially the same as are produced by other alkalies.

To understand the behavior of phenol-phthalein and other indicators a word about their constitution will be in order. These substances are in general very weak bases or very weak acids, and weaker than the acids and bases with which they are to be used. In addition to

this the characteristic ions which they contain must have one color in the dissociated condition and a different color in the non-dissociated condition. Phenol-phthalein in presence of even very weak acids is non-dissociated and colorless, but with sodium hydroxide the sodium salt is formed, which like other salts is more or less dissociated. The separated phenol-phthalein ion possesses a red color. This red color comes at once only with relatively strong bases; with ammonia, on the other hand, which is a weak base, an appreciable excess must be used to strike a red color. This is due to the fact that the salt formed by combining the weak ammonium with the weak phenol-phthalein ion suffers, at first, hydrolytic decomposition in the solution with immediate loss of color. To overcome this more ammonia must be added, until finally a little dissociated ammonium phenol-phthalein persists. Methyl orange acts as a weak base, which in the undissociated condition is yellow; when combined with the stronger acids salts are formed, and in these the dissociated organic ion is red. This indicator can not be used with very weak acids, and mainly for the same reasons given for the lack of delicacy of phenol-phthalein with very weak bases like ammonia.

The production of sodium hydroxide from the carbonate is illustrated by the next experiment.

Experiment 155. Dissolve 50 Gm. of common crystallized sodium carbonate in 250 Cc. of water in a porcelain dish, and add *milk of lime* made by mixing 25 Gm. of slaked lime with 75 Cc. of water. The milk of lime is to be added slowly to the boiling solution of the carbonate, the mixture being well stirred during the addition. After the lime has been all added, boil the mixture about ten minutes, keeping it well stirred. Filter the liquid portion through a plug of asbestos in the apex of a funnel and then pour on the sediment in the dish. When the liquid has drained from this, add a little water to the funnel to wash out more of the product. Test a portion of the filtrate with hydrochloric acid. It should give no effervescence from presence of unchanged carbonate. Evaporate the remainder in a porcelain dish and observe that a white residue of soda is left. During the evaporation this takes up some carbon dioxide from the air and becomes partly carbonate again.

On the large scale this reaction is carried out in iron

boilers. The hydroxide solution, separated from the sediment, is boiled down in kettles, and when ready to solidify is poured into iron drums for shipment in large lots or into molds for formation of smaller lumps. Some is cast in stick form for laboratory use. In chemical industry the hydroxide is employed in making soap by the saponification of fats; also in the production of many organic coloring matters, and for minor purposes. The commercial article usually contains a little water.

Several other methods of producing soda have been tried. The following experiment will illustrate the principle involved in a method which promises at the present time to make great changes in the alkali industry, and which is already in successful operation on the large scale.

Experiment 156. Nearly fill a large U-tube with a strong solution of sodium chloride. Into each limb of the tube dip thin pieces of platinum foil, about 1 Cm. wide and 5 Cm. long. These pieces of platinum are fastened to platinum wires, which in turn are attached to copper wires leading from the poles of a galvanic battery of five or six Daniell or equivalent elements. Just before making the last attachments pour a few drops of solution of phenol-phthalein into the limb connected with the zinc pole of the battery, and some indigo solution into the other limb of the U-tube. Now complete the connection with the battery, and observe that the salt solution in the side with the phenol-phthalein soon turns bright red, showing formation of alkali, while the indigo solution in the other limb is gradually bleached by chlorine liberated, the odor of which can be readily detected. The electric current passing through the solution decomposes the salt, separating the sodium from the chlorine. The latter is liberated on one plate, or *electrode*, while the former decomposes water at the other, producing caustic soda. On the large scale it has been found possible to separate and save the soda so formed, powerful currents from dynamos being employed.

Sodium Carbonate. This substance, mixed with sodium sulphate, is found in great deposits in Wyoming and other parts of the United States. As no easy method of purification has yet been discovered, this crude soda has been utilized to a limited extent only.

Leblanc Process. The commercial carbonate is produced by two essentially different processes at the present

time. The older of these is known as the Leblanc process and depends on these reactions. Common salt is converted into sulphate by the action of strong sulphuric acid:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

The sulphate is roasted with a mixture of coal dust and limestone. The first reduces sulphate to sulphide:

$$Na_2SO_4 + 4C = Na_2S + 4CO$$

The second then converts sulphide into carbonate:

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS$$

The first one of these reactions is conducted in a reverberatory furnace so constructed that the hydrochloric acid may be led off into Woulfe bottles and condensed, or, more commonly into coke towers and there condensed by water flowing down over the coke. The sulphate is thoroughly roasted to expel all acid and in this form is known as *salt cake*. This is broken into lumps and introduced into a second furnace with the coal and limestone. This may be a reverberatory furnace also, and is commonly called a black-ash furnace, because the three substances on thorough roasting yield a black mass. At the end of the process this is raked out, cooled and leached with water. The calcium sulphide is not soluble in the alkaline liquid while the carbonate dissolves readily, with several by-products. The leach liquor is evaporated to crystallize the carbonate which is deposited in the form of sal soda, $Na_2CO_3.10H_2O$. A large part of this product is calcined to drive off the water. The residue is known as soda ash and is largely used in the production of common glass. A part of the sal soda is purified by recrystallization and is used in making many pharmaceutical products. It is also used, as shown above, in making caustic soda. Some of the important properties of the sal soda may be learned from the following experiment:

Experiment 157. Let the student make some experiments with a large crystal of sal soda. Break it into small pieces. Heat some of these in a porcelain dish and observe that they melt to a liquid mass which gives off water by continued heating, leaving finally a white powder. Dissolve some of the fragments of the crystal soda in water. Notice the taste of the solution by bringing a small drop on a glass rod to the tongue. Test the reaction of the solution with litmus and phenol-phthalein. Pour some dilute hydrochloric acid into a little of the solution in a beaker. A gas is given off. What is it? Continue the addition of the dilute hydrochloric acid until no more gas escapes on shaking, then evaporate the solution to complete dryness in a porcelain dish. Taste the residue. What is it? Into some more of the solution of the crystals to which a little phenol-phthalein has been added, pass carbon dioxide gas from a generator until the color disappears. Sodium *bicarbonate* is here formed.

Solvay Process. The largest part of the carbonate of commerce is now made by a process known as the Solvay process or ammonia process. This is the result of attempts to decompose salt directly without the aid of the sulphuric acid, and depends on the reaction:

$$NaCl + CO_2 + NH_3 + H_2O = NH_4Cl + HNaCO_3$$

Strong brine is saturated with ammonia gas and then treated with carbon dioxide in tall tanks under pressure. As the ammoniacal brine becomes saturated a fine granular precipitate of sodium bicarbonate forms and gradually sinks to the bottom of the reaction tanks. This continues until a large part of the salt is decomposed. The bicarbonate is now removed, washed with cold water saturated with the same salt, dried and calcined to produce soda ash. The CO_2 given off is utilized for saturation again. The success of the process depends on the fact that from the NH_4Cl left in the mother liquor the whole of the ammonia may be recovered, by boiling with slaked lime, and used over again with fresh brine.

Sodium Bicarbonate. As shown at the conclusion of the last experiment, sodium bicarbonate is formed when carbon dioxide gas is led into a solution of the carbonate, or when the gas is brought in contact with lumps of partially effloresced sal soda:

$$CO_2 + Na_2CO_3 + H_2O = 2HNaCO_3$$

As the behavior with the phenol-phthalein shows, this is not an alkaline substance. It is made in great quantities for use in the manufacture of baking powders, effervescing mixtures and other medicinal products.

Experiment 158. Let the student mix a small amount of finely powdered "cream of tartar" (an acid substance), with some sodium bicarbonate on a sheet of paper. No change is apparent. Then throw the mixture into a beaker and add some water. A lively effervescence follows. This is from the escape of the CO_2, set free by the action of the acid substance on the bicarbonate in presence of water.

Sodium Chloride, or common salt, is the most abundant of the sodium compounds. It is obtained from deposits of rock salt found in many parts of the world, from brine springs, and from sea water. In very cold latitudes this is concentrated to a point where boiling is economically possible by freezing the water pumped up into large shallow basins. In freezing little of the salt separates with the ice. The operation is repeated several times, until the greater part of the water is removed. In tropical or semitropical countries water is pumped from the ocean or allowed to flow at high tide into basins, where evaporation takes place by the sun's heat. The brine of many springs is strong enough in salt to pay for direct concentration over fire. After separation of most of the salt the mother liquor is used for the manufacture of bromides, which in many places is an important industry. As shown above, salt is used in making other important sodium compounds. It dissolves in somewhat less than three parts of water at the ordinary temperature.

Sodium iodide, NaI, and *sodium bromide,* NaBr, are analogous compounds, used mainly in medicine.

Sodium Sulphite is a soluble salt, made by passing SO_2 into a solution of the carbonate to saturation, after which an equal amount of carbonate is added, and the whole allowed to stand to crystallize as $Na_2SO_3.7H_2O$. The salt is used for several purposes, and very commonly as a constituent of developing solutions in photography, on account of its reducing properties. The acid sulphite, $HNaSO_3$, is also used in photography.

Sodium Sulphate. This is a very common substance made by the action of sulphuric acid on common salt. In the crystalline form, $Na_2SO_4.10H_2O$, it is known as Glauber's salt. A partially effloresced product is found in large deposits in the western part of the United States. The dried sulphate is often used in the place of the carbonate in making glass, but a higher heat is required in the fusion.

Sodium Thiosulphate, $Na_2S_2O_3.5H_2O$, is made in large quantities for use in photography as a fixing agent, and to remove excess of chlorine after bleaching in the paper industry. Its action in photography will be explained later.

Sodium Nitrate. This important compound is found in large deposits along the western coast of South America and is known as Chili saltpeter. In crude form it comes into commerce for use as a fertilizer. After refining it is employed in making nitric acid and in making potassium nitrate, to be presently explained. Large quantities are also used in the manufacture of gunpowder.

Sodium Nitrite. This salt is usually made by fusing the nitrate with metallic lead, which takes out some of the oxygen. The nitrite is used in enormous quantities for the manufacture of certain organic chemicals, and in chemical analysis as a reagent.

Among other important compounds of sodium there are borax, $Na_2B_4O_7.10H_2O$, and sodium silicate or water-glass, Na_2SiO_3, described in the ninth chapter and the phosphates, described in the tenth chapter. Sodium dichromate, $Na_2Cr_2O_7$, is an important salt which will be referred to later.

Recognition. Sodium compounds are easily recognized by the intense yellow color they impart to the flame of the Bunsen burner and by the bright yellow line seen with the spectroscope, to be explained in Chapter XVI.

POTASSIUM.

Occurrence. Found very widely distributed in rocks and soils. As potassium carbonate it occurs in the ashes

of plants. Potassium chloride, KCl, occurs as *silvine* in the famous salt deposits of Stassfurt, Germany, along with *carnallite*, $KCl.MgCl_2.6H_2O$. A large part of the potassium compounds of commerce is made from these minerals. Potassium nitrate appears as an efflorescence on many soils in hot climates, and at one time this was a very important source of the crude niter used in Europe.

History. What was said about sodium applies to potassium. It was isolated in 1807 by Davy from potassa, in which the presence of a metal was not suspected. The compounds we call potassa and soda were supposed to be simple substances by most chemists, although Lavoisier had suggested that they must contain oxygen.

Manufacture. The reactions given for sodium apply here as well. In the early aluminum industry potassium was employed as the reducing agent, but because of its much greater atomic weight was later displaced by sodium which could be produced even more readily. At the present time potassium is not manufactured in large quantities.

Properties. A soft white metal which tarnishes readily, burns when heated in the air and decomposes water with liberation of hydrogen. In general its behavior is much like that of sodium.

Uses. It is employed sometimes in scientific investigations and in the preparation of the pure hydroxide for experimental purposes.

The compounds of potassium closely resemble those of sodium.

Oxides. Two oxides, K_2O and K_2O_4, are well known but not technically important. Several other oxides have been described.

Potassium Hydroxide. The pure substance may be made by the action of potassium on water,

$$K + H_2O = KOH + H,$$

but is commonly made by the decomposition of potassium carbonate by slaked lime as described under sodium:

$$K_2CO_3 + CaO_2H_2 = CaCO_3 + 2KOH$$

The $CaCO_3$ we are already familiar with as calcium carbonate, identical in composition with marble and pure limestone. It is insoluble in water, and at the end of the decomposition remains in the sediment with the excess of CaO_2H_2 taken.

Potassium hydroxide is employed for many purposes in the arts, especially in the manufacture of soft soap and certain organic coloring substances. For laboratory and pharmaceutical uses it is sold in the form of sticks, for convenience in handling. This product is not pure KOH, but contains always 10 to 15 per cent of water, with some foreign substances.

Potassium Carbonate. This very important compound is produced on the large scale in several ways, but only one method of manufacture will be illustrated here. Wood ashes contain notable quantities of the carbonate which can be extracted with water. The solution obtained yields on evaporation a crude carbonate.

Experiment 159. Pour lukewarm water over several hundred grams of fine wood ashes in a large beaker. Enough water should be taken to make a thin mixture easily filtered. After stirring the mixture thoroughly filter it through a large filter, or better, through a plug of asbestos in the neck of a funnel. The filtrate will have a brownish color. Evaporate it to dryness in a porcelain dish. The residue obtained contains a large proportion of potassium carbonate, with other soluble salts from the ash, as potassium sulphate, potassium chloride, potassium silicate and other products in smaller amount. Test the alkalinity of the substance by means of litmus or phenol-phthalein, and try the behavior with acids.

The crude potash may be partially purified by heating very strongly to destroy organic matters present. The dry product is dissolved in twice its weight of water, filtered, the filtrate evaporated to one third its volume and allowed to stand. Most of the sulphate and some other salts settle out. The remaining liquid is evaporated until

the carbonate begins to crystallize, and is then allowed to cool and deposit most of it. This product is collected, dried and strongly heated to drive off more water, and yields then what is known as *pearl ash* or *refined potash.* Much of the carbonate of commerce is now made by the Leblanc and Solvay processes as described under sodium.

When perfectly dry it is used to absorb water from certain liquids, as commercial alcohol, to dry gases, and for other purposes depending on its power of attracting moisture. This power can be tested by exposing some of the dry product to the air for several days.

The carbonate is used in the manufacture of the hydroxide, as stated, and also in making certain kinds of glass. Hard glass is essentially a combination of the silicates of calcium and potassium obtained by melting together sand, lime and calcined potash.

Potassium Chloride. The native mineral is found in nearly pure condition, and by recrystallization is made ready for laboratory use. It serves as the starting point in making other potassium salts, just as common salt serves for the sodium compounds.

Potassium Iodide and Bromide are important substances used in medicine. They are produced from free iodine and bromine by several reactions, which cannot be described here.

Potassium Sulphate is made by the action of sulphuric acid on the chloride. It is used for several purposes in the laboratory, and on the large scale serves for the preparation of potassium carbonate by the Leblanc process.

Potassium Nitrate. The important properties of this substance were explained when nitric acid was studied. It is very soluble in water, easily melted, and is readily decomposed by sulphuric acid, yielding nitric acid and potassium sulphate. When mixed with sulphur and charcoal it gives up oxygen readily under certain conditions and often with explosive suddenness. Hence its use in gunpowder and fireworks mixtures.

It is manufactured in great quantities and generally by decomposition between potassium chloride and sodium nitrate:

$$KCl + NaNO_3 = KNO_3 + NaCl.$$

The reaction depends on the facts that potassium nitrate is very soluble in hot water and much more soluble than sodium chloride, and further that the latter is not much more soluble in hot water than in cold. The manufacture is carried out in various ways: sometimes by mixing the chloride and nitrate in molecular proportions, that is 74.6 parts of KCl to 85 parts of $NaNO_3$, and adding this mixture to boiling water as long as it all dissolves. When a condition of saturation is reached the liquid is allowed to cool. A large amount of KNO_3 crystallizes out, while nearly all the NaCl produced stays in solution. The saltpeter is then easily purified by recrystallization from water. A more common method is to add the molecular mixture to boiling water, usually the water from which saltpeter has been recrystallized in previous operations, until a specific gravity of 1.5 is reached. Sodium chloride is precipitated in this way and the supernatant liquid drawn off deposits the potassium nitrate on cooling.

Potassium Chlorate. This salt is usually made by a series of reactions which are somewhat complicated. When chlorine gas is passed into a strong, hot solution of potassium hydroxide this change takes place:

$$3Cl_2 + 6KOH = 5KCl + KClO_3 + 3H_2O.$$

and in this manner the salt was formerly made, being easily separated from the KCl by crystallization. At present the much cheaper substance milk of lime, CaO_2H_2, is converted in the same way into calcium chlorate, $Ca(ClO_3)_2$. The solution is concentrated and treated with KCl which brings about a double decomposition, because potassium chlorate is less soluble than calcium chlorate:

$$Ca(ClO_3)_2 + 2KCl = 2KClO_3 + CaCl_2$$

The chlorate is easily purified by crystallization, as it is not very soluble in cold water.

This salt, like the nitrate, is valuable mainly because of its power of furnishing oxygen. Hence its use in the manufacture of oxygen gas, already illustrated. In the manufacture of explosive mixtures and of fireworks it plays an important part. Some formulas are here given illustrating the production of these mixtures for colored fires:

White.	
Potassium nitrate	16 parts.
Antimony sulphide (natural)	6 "
Sulphur	4 "
Red lead	5 "

Violet.	
Potassium nitrate	16 parts.
Potassium chlorate	14 "
Chalk	10 "
Sulphur	10 "
Lampblack	0.5 "

Green.	
Potassium chlorate	3 parts.
Barium nitrate	8 "
Sulphur	3 "

Blue.	
Potassium chlorate	6 parts.
Ammonia copper sulphate	8 "
Shellac	1 part.

Red.	
Potassium chlorate	3 parts.
Strontium nitrate	18 "
Shellac	6 "

In all cases the materials used must be dry, and must be *powdered separately*. The proper weights of the different substances are then mixed, without rubbing, best on a sheet of paper, with the hand. It will be observed that either the nitrate or chlorate of potassium appears in each one of these formulas.

Among other important potassium salts the chromate and dichromate must be referred to. More will be said about them in the chapter on chromium. The permanganate will also be described later.

Recognition. Potassium compounds are recognized by the violet color they impart to the Bunsen flame, by the bright red line they exhibit in the spectroscope and by a yellow precipitate formed under certain conditions with platinum chloride.

RUBIDIUM AND CÆSIUM.

These are two rare metals found in a number of minerals, but not in large amount. They are found in traces in many mineral waters and it was in the examination of such waters by the spectroscope that they were discovered in 1860 and 1861 by Bunsen. Cæsium is characterized by showing two bright blue lines and rubidium by a number of lines, among them two in the deep red end of the spectrum.

AMMONIUM COMPOUNDS.

It has been explained already that ammonia, a gaseous substance represented by the formula NH_3, is obtained usually from certain by-products formed in the manufacture of illuminating gas. These by-products appear as salts of *ammonium*, NH_4, a hypothetical combination not known in the free state, but assumed to exist in union with other elements in the form of salts. The general behavior of these salts has been shown by experiment. They are volatile, some being decomposed at the same time. They are nearly all extremely soluble in water, and all are decomposed when boiled with strong alkali solutions. We can apply these facts to the detection of ammonia in mixtures.

As was shown in the first pages of this book ammonium chloride vaporizes without melting to the liquid condition. This is possibly due to the fact that at a moderately high temperature it suffers dissociation, that is, it decomposes into NH_3 and HCl. These gases may be actually separated in properly constructed apparatus. In ordinary sublimation vessels, however, they recombine, when a point is reached where the temperature is low enough. This dissociation offers a good illustration of a reversible reaction,

$$NH_4Cl \rightleftarrows NH_3 + HCl$$

The most important of the ammonium salts are the chloride, the nitrate, the sulphate and the carbonate. The first three are usually made by direct combination of ammonia water with the corresponding acids. The com-

mercial carbonate of ammonium is a mixture of the bicarbonate or acid carbonate, $H(NH_4)CO_3$, with ammonium carbamate, $(NH_4)NH_2CO_2$, and is usually made by subliming a mixture of ammonium chloride and chalk. When this is dissolved in water with the addition of ammonia the true normal carbonate, $(NH_4)_2CO_3$, is formed.

By saturating ammonia water with hydrogen sulphide gas a solution is obtained which contains $(NH_4)HS$. This is much used as a laboratory reagent. By adding to this solution an equal volume of the ammonia water the sulphide, $(NH_4)_2S$, is formed. Both solutions have applications in analytical chemistry and both decompose on standing.

Recognition. Ammonium compounds are readily recognized by the liberation of ammonia when they are boiled with milk of lime or other fixed alkali solution. NH_3 is the only common volatile alkali. Among organic compounds there are known a large number of bodies called amines, or compound ammonias, which show some of the properties of ordinary ammonia; but as they are not commonly met with, they are not liable to be mistaken for the inorganic ammonium salts.

CHAPTER XV.

THE COPPER GROUP: COPPER, SILVER AND GOLD.

GENERAL CHARACTERISTICS.

The metals of this group are not as closely related as are those of the alkali group, yet they show in their physical properties and in the properties of their compounds many analogies. As metals they resemble each other in their extreme malleability, ductility and position of their melting points. In many of their compounds they are univalent, and in this they resemble the alkali metals. Solutions of their compounds are very readily electrolyzed with precipitation of the pure metals. The following table exhibits important physical properties:

	Atomic Weight.	Specific Gravity.	Atomic Volume.	Melting Point.	Boiling Point.
Copper	63.60	8.95	7.10	1045°	White heat.
Silver.....	107.93	10.55	10.23	945°	"
Gold.....	197.20	19.30	10.22	1035°	"

COPPER.

Occurrence. The metal is found in large quantities in the free or native condition, especially in the Lake Superior mines. In combination the common ores are copper pyrites, $CuFeS_2$; copper glance or vitreous copper ore, Cu_2S; malachite, $CuCO_3.CuO_2H_2$; red copper ore, Cu_2O; and gray copper or tetrahedrite, $4Cu_2S.Sb_2S_3$. Many other ores of less importance are known, and these cited are seldom found in the pure condition indicated by the formulas, but are often mixed with sulphides of other substances as cobalt, nickel, silver and arsenic. The largest part of the copper of commerce comes from the

native ore and the copper pyrites. The most productive deposits are those of Cornwall, the Siberian mines in the Ural Mountains, the mines of Chili, of southern Australia, of Saxony and the Harz region in Germany, of Spain and especially of the Lake Superior, the Montana and the Arizona mines in the United States. At the present time over one half of the world's supply of copper is produced in this country. In 1903 the total production was 582,243 metric tons, that of the United States being 312,532 metric tons.

History. Copper has been known and used since the earliest historical times and was employed largely in the production of bronze by the Greeks, Romans and Egyptians. Articles of bronze, as tools and weapons, were far more common, at one time, than those of iron and steel.

Metallurgy. The production of pure copper from the native Lake Superior ore is largely a mechanical operation. The ore containing the free copper is crushed in stamp mills and the fine product so obtained is systematically washed to carry away the lighter rocky or earthy materials, leaving the heavy copper behind. Much of this native copper is in large masses which simply require fusion to be brought into marketable condition. But most of the metal exists in a finely divided condition with clay or rock and this requires separation by crushing and washing. The thoroughly washed ore is finally fused with a little carbon to prevent oxidation and cast into bars or ingots. This copper is very pure and is valued because of its freedom from other metals.

A very large proportion of the total production of copper comes from the several sulphides smelted. The reactions involved are somewhat complicated, but may be briefly described in this way: The ores are roasted in the air, by which means a part of the sulphur is expelled as SO_2, and some arsenic and other impurities are lost. This roasted ore is then fused in blast furnaces or reverberatory furnaces with coke and slag from previous operations. Much of the iron separates as silicate in the slag formed, while the copper is practically all left as sulphide. There must always be sulphur enough present for this purpose, otherwise copper would also be lost in the slag. This latter does not mix with the sulphide readily and is separated mechanically. The

impure copper sulphide is called the regulus and is next subjected to repeated oxidations, by which most of the sulphur is burned away, leaving a mixture of Cu_2O and Cu_2S. By properly conducting the oxidation the proportions of these can be controlled so that by increasing the heat of the furnace they will react on each other in this way:

$$Cu_2S + 2Cu_2O = 6Cu + SO_2$$

Metallic copper with several impurities, and known as *coarse copper*, is thus secured. This is melted in the air so that the traces of arsenic, antimony, sulphur, iron, lead and other substances oxidize and escape in the gaseous condition or form a slag with the silica of the furnace hearth. This is possible because all these elements oxidize very much more readily than does copper. However, a small amount of red oxide of this metal is formed and a little sulphide still remains. To effect final purification the molten metal is covered with powdered charcoal and is then stirred with poles of green wood, which give off water vapor and reducing gases. These combine with the oxygen and sulphur and leave the copper in practically pure condition. This final operation is known as *poling* the copper.

In many places at the present time the coarse copper is refined by a process of electrolysis. The impure metal is cast in large plates which are hung as the anodes in a bath of copper sulphate with a little sulphuric acid. The cathodes consist of thin sheets of copper. On passing the current, practically pure copper deposits on these sheets, which thus grow up into bars. The copper only of the anodes is taken up, as lead and other impurities are left insoluble, or oxidize and settle to the bottom of the refining vats. This electrolytic copper is almost absolutely chemically pure.

Properties. Pure copper is extremely ductile and malleable; it is, next to silver, the best conductor of heat and electricity, and is but slightly oxidized in either dry or moist air. It alloys readily with many other metals. Its specific gravity is over 8.9, and its melting point is slightly above 1,000°.

Uses. It is employed largely in the form of sheets for making water-baths, air-baths, stills and kettles for use on the large and small scale. Also in enormous quantities in the form of wire for electric conductors. It is a constituent of several valuable alloys. Bronze is an alloy of copper and tin in various proportions from 95 of copper and 5 of tin to 75 of copper and 25 of tin. Some

kinds of bell metal have about the latter composition. Brass is an alloy of about 2 parts of copper to 1 part of zinc. Aluminum bronze contains usually 90 parts of copper to 10 of aluminum. German silver is an alloy of copper, zinc and nickel.

Copper forms two classes of compounds, known as cuprous and cupric. In the first the metal behaves as an univalent element while in the second the condition is bivalent. The cupric compounds are more numerous and important than the cuprous.

Copper Oxides. Two are known, the cuprous oxide or red oxide, Cu_2O, and the black cupric oxide, CuO. The first is prepared by heating a mixture of black oxide and copper filings in equivalent proportions, or by the reduction of an alkaline cupric solution by means of a solution of dextrose, which was illustrated in an experiment in the chapter on carbon. The cuprous oxide is bright red and is employed in the coloring of glass; a little of it added to the ordinary colorless glass in the melting pots converts it into ruby glass. The black oxide, CuO, may be made by the oxidation of metallic copper and by the decomposition of the nitrate by heat. It is sometimes used in coloring glass light green, and is employed commonly as an oxidizing agent in organic combustion analyses. This oxide dissolves in acids yielding the cupric salts, which are blue or green.

Copper Hydroxides. Cuprous hydroxide is known as a yellow precipitate. Cupric hydroxide is obtained as a green precipitate by adding an alkali solution to a solution of copper sulphate or other cupric salt. This precipitate dissolves in ammonia water with a deep blue color. It is also soluble in solutions of many organic substances as the sugars, glycerol, tartrates and mannitol. The solution in Rochelle salt constitutes the ordinary Fehling solution employed in sugar tests.

Copper Chlorides. Cuprous chloride, CuCl, or Cu_2Cl_2, is obtained as a white powder, insoluble in water, by heating a mixture of cupric chloride and hydrochloric acid

with scrap copper; on dilution with water the white precipitate appears. It dissolves in ammonia and this solution has important applications in gas analysis. Cupric chloride, $CuCl_2.2H_2O$, is a green, soluble crystalline compound, produced by dissolving the black oxide in hydrochloric acid. It is also used in analytical chemistry.

From analogy with several other bodies cuprous chloride is usually considered as having the composition CuCl, but a determination of the vapor density leaves the matter somewhat in doubt.

Copper Sulphate. The most important of the copper compounds is blue vitriol, $CuSO_4.5H_2O$, which may be made by the solution of the black oxide in sulphuric acid, but is also largely made as a by-product in several metallurgical processes. It is readily soluble in water and serves as the starting point in the preparation of several other copper compounds. The present annual production of the United States is about 25,000 tons.

A solution of blue vitriol is employed in copper electroplating and in electrotyping, the metal being deposited on a surface by electrolysis. In this manner a firm coating of copper may be put on iron or other metals. Or a coating, *which may be stripped off*, may be deposited upon a wax or plaster of Paris cast, thus giving a copy of the original. This important process will be illustrated by an experiment.

Experiment 160. Prepare a wax copy of a medal in the following manner: Melt together about 100 Gm. of beeswax, 5 Cc. of oil of turpentine and 10 Gm. of very fine graphite powder. Stir thoroughly to distribute the graphite uniformly. Next, brush fine graphite over the surface of the medal to be copied, and then wrap a strip of paper around its edge so as to form a cell a centimeter or more in depth, the bottom of which is formed by the medal; support the paper strip with a rubber band. Then allow the wax to partially cool, stirring it meanwhile, and just before it begins to become stiff pour enough into the cell to half fill it. Then lay a piece of copper foil, to which an insulated copper wire about 15 Cm. in length is soldered, on the wax and add more of the melted wax to quite fill the cell, which is next set aside until the contents become hard. On unwinding the strip of paper, the wax may be readily detached from the surface of the medal, and on its under surface will be found a sharp im-

pression of the latter. Sprinkle some fine graphite on this wax surface, and by means of a soft, but closely filled camel's hair brush, rub the graphite over the whole surface so as to impart a high polish to it. If the wax is of the proper degree of hardness this can be easily done with a soft brush, having short, close hair. When the polish is perfect and uniform wash off the loose graphite remaining, under flowing water, and pour a 10 per cent copper sulphate solution over the polished surface. Distribute this evenly by means of a very small brush. Then add some fine iron filings, *free from grease*, and mix them thoroughly with the copper solution. By this means a thin coating of pure copper is deposited evenly over the polished surface by precipitation. Add more solution and filings, if necessary, to make this complete. Then wash thoroughly in flowing water and, without delay, suspend this prepared wax copy in a 20 per cent solution of copper sulphate, slightly acidulated with sulphuric acid. Attach the insulated copper wire leading from the plate in the center of the wax, to the zinc pole of a battery of five or six Daniell or equivalent elements and lead the current from the battery into the solution by means of an insulated wire soldered to a plate of copper. Suspend this plate so that it stands parallel to, and about half a centimeter away from the coppered surface of the wax cast. Under these conditions copper will be deposited from the solution on the cast and taken by the solution from the copper plate. At the end of about 24 hours a fine layer of pure copper will be found on the wax, and can be readily lifted from it. It will be seen that an accurate copy of the original medal has been made by the copper, the wax copy being a reversed one. Any desired thickness of the copper may be deposited by giving more time to the process. The addition of graphite to the wax makes it a conductor of electricity and prevents its permanent adherence to the metal. By a slight modification of the process illustrated, an electrotype copy of a page of type may be made, and this may be used in place of the real type in printing.

Blue vitriol when carefully heated loses all of its water of crystallization and leaves a white powder of the pure sulphate, $CuSO_4$. When this is exposed to moist air it absorbs water and becomes blue. It is also employed as a test substance for the presence of water in alcohol and certain other organic liquids. In absolute alcohol the anhydrous sulphate remains white, but if a very small amount, even, of water is present, it becomes blue after a time. Ammonia is absorbed by anhydrous copper sulphate, forming a blue compound with the formula $CuSO_4.5NH_3$, which by heat is changed to $CuSO_4.NH_3$. A crystalline compound, $CuSO_4.4NH_3.H_2O$, is also known.

Copper Arsenite is formed by precipitating a solution of copper sulphate with one of sodium or potassium arsenite. This is a very poisonous substance and is commonly known as Scheele's green. A somewhat similar green precipitate is formed by mixing a boiling solution of copper acetate with a boiling solution of arsenous acid. This product is known as Schweinfurt green.

Recognition. Copper compounds are easily recognized by the precipitation of the metal on a strip of bright iron from a solution of the sulphate or other salt, by the deep blue color produced by the addition of ammonia in excess to copper solutions, and finally by the red precipitate of copper ferrocyanide, $Cu_2FeC_6N_6$, produced on the addition of potassium ferrocyanide to a neutral or slightly acid copper solution.

SILVER.

Occurrence. Silver is found in small quantities in the uncombined condition, but it usually occurs as sulphide with lead, arsenic and antimony, and occasionally as chloride. Of the sulphides silver glance ore, Ag_2S, red silver ore, Ag_3AsS_3, and brittle silver ore, $5Ag_2S.Sb_2S_3$, are the most important; but many deposits of galena, PbS, contain silver as sulphide, and much of the silver of commerce comes from this source.

The most productive silver regions of the world are those of the western United States, Mexico, Bolivia and Australia.

The world's total production of silver in 1903 was 5,201,545 kilograms. Of this the United States furnished 1,088,005 kilograms, Mexico 2,100,818 kilograms, Bolivia 233,274 kilograms, Australia 370,110 kilograms and Germany 181,020 kilograms.

History. Silver has been known from the earliest times, and has always been highly prized on account of its color and valuable property of alloying with other metals. The amount of silver known to the ancients was, however, very small as compared with the amounts now in use.

Metallurgy. Silver is separated from its ores by several methods, of which the two most important will be briefly described.

Amalgamation Process. This is a process in which silver is taken up by mercury from the ore after preliminary treatment. This treatment varies in different localities, and in many cases no simple explanation can be given of the chemical principles involved in it. Often the ore is crushed and roasted with common salt to convert sulphide into chloride of silver. The finely ground product is agitated with water and scrap iron, by which the chloride of silver is reduced to the metallic condition. Mercury is added and thoroughly mixed with the mud formed for several hours, until the amalgamation or solution of the silver in the mercury is practically complete. This operation is carried out in large tanks, and when finished water is run in to wash away the lighter mud, leaving the heavy amalgam at the bottom. The amalgam is gathered up, pressed into balls, dried and distilled from a retort, by which means the mercury is recovered for further use and the silver left in metallic condition, ready for the refiner. In some cases the amalgamation is conducted without the preliminary roasting of the ore, and it is also possible to reduce the silver chloride in the amalgamation process itself, without the use of scrap iron. As silver ores often contain gold, this metal will be left with the crude silver in the retort. The method of refining will be explained under gold.

Smelting Process. As silver ores usually contain lead it has been found most economical and simple to combine the reduction of the two metals by a smelting process, the important principle involved being this: Lead ores, by the addition of proper fluxes, may be easily reduced in a blast furnace by coke to the metallic condition. This reduced lead in turn acts on the silver and gold compounds, reducing them likewise to metals and alloying with them. The molten lead then settling to the bottom of the blast furnace carries the other metals, and from time to time is run off into molds, forming pigs, from which the metals present may be separated by subsequent operations. The smelting operation is usually preceded by a roasting to remove a large part of the sulphur and form lead oxide. It is customary to charge the blast furnace with a mixture of ores rather than with a single one, in order to secure by the proper combination of acid and basic material a charge which will flux easily, that is, in which the heavy metals will separate perfectly from the other substances left as a slag.

The crude lead from the smelting furnace is known as base bullion and is treated for separation of the several metals in it. The principal steps in the process can be only briefly described. The bullion is heated on the hearth of a reverberatory furnace and stirred thoroughly to bring every part in contact with air. This suffices to oxidize several metals which may be present in

small amount, and separate them as a dross which may be removed by skimming. Antimony, copper and arsenic are so separated. What is left is generally treated by the Parkes process. The metal is melted in large iron pots and a small amount of zinc, 1 to 2 per cent by weight, is added and thoroughly incorporated by stirring. Zinc combines readily with silver and gold, but only in limited proportion with lead. The zinc therefore separates, comes to the surface, carrying with it the precious metals. The whole mass is allowed to cool slowly and the zinc alloy on the surface begins to solidify first. It is skimmed off with a perforated ladle and transferred to a separate vessel. To the residue of lead more zinc may be added, a second and third time if necessary, which is determined by the richness in silver of the original bullion, the main portion of which is lead, of course. A very little of the zinc remains with the lead, while the other metals are practically all removed. From the large mass of lead the trace of zinc is removed by heating to a high temperature, as zinc volatilizes readily. It remains to separate the precious metals. To this end the zinc alloy is heated in graphite crucibles or retorts to such a temperature that the zinc distills out almost completely and is condensed for use again. The residue contains lead with the precious metals and the former is eliminated by oxidation in a current of hot air, the lead being converted into litharge, a little of which is absorbed by the hearth of the cupel furnace in which the oxidation is conducted, the most being floated off as a molten slag from the top of the heavier metal. This litharge is later reduced to lead.

The metal now remaining consists of silver mainly, with a little gold, and possibly traces of other metals. The separation of these will be described a few pages in advance, under gold. It has been recently discovered that a minute amount of aluminum added with the zinc in this process aids materially in the separation of the silver and gold from the lead. Other methods and modifications are used in various places; but the details cannot be explained here.

Properties. Silver is the best known conductor of heat and electricity, is very malleable and ductile, and alloys readily with many metals. At a high temperature it absorbs gases in large volume, to give them out on cooling. The metal is not dissolved by hydrochloric or dilute sulphuric acid, but is dissolved by strong hot sulphuric acid and by nitric acid.

Colloidal Silver. Like several other metals silver may be readily obtained in the form of a colloidal solution in water. This is most conveniently done by making an electric arc between two poles of silver wire beneath the

surface of distilled water. Silver goes into solution in colloidal form. The liquid becomes purple and possesses very peculiar properties. Somewhat similar solutions are made from platinum and copper. In this form the metals are often spoken of as inorganic ferments.

Uses. The metal is largely used in coinage, alloyed with copper to harden it. In this country the alloy contains 90 parts of silver to 10 of copper. In solid silverware the metal is alloyed in the same manner, but often with more copper. Immense quantities of silver are employed in plating by a process essentially similar to that illustrated under copper. The silver plating bath is a solution of silver cyanide in an excess of potassium cyanide, and is made in various ways. Any amount of silver may be deposited on copper, brass, pewter and certain other alloys, but in practice the thickness of the film is not great. A film having a thickness of 0.01 Mm. is practically a good one. This contains about 1 gram of silver to the square decimeter. Three grams of silver on a square decimeter is a very good plate and has the thickness of thin writing paper.

All articles to be covered must be thoroughly cleaned first, by immersion in a hot alkali solution in case of Britannia metal or pewter, and in nitric acid in the case of copper or brass. These baths remove the impurities on the surfaces to be covered. The articles are then thoroughly washed and suspended in the plating solution. But many details in the process of washing which cannot be explained here must be observed. It is absolutely necessary to have the surface perfectly clean and free from oxide, scale or impurity of any kind.

Plating Solution.

As it may interest the student to have the composition of a good plating bath, the following figures are given: Dissolve 17 Gm. of silver nitrate in about 150 Cc. of water. Make a solution of 10 Gm. of commercial potassium cyanide in 100 Cc. of water and mix the two solutions, stirring well. Allow to settle and then pour off two portions of the clear liquid of about 25 Cc. each. To one add a few drops of dilute silver nitrate solution. If a precipitate forms here it shows that too much cyanide had been added. In this case return both portions to the main liquid and add a little more silver solution as long as a precipitate ap-

pears to form. On the other hand, if the silver nitrate solution does not make a precipitate, add a little cyanide solution to the second small portion of liquid poured. A precipitate should show here, indicating an excess of silver in the mixture. Return both small portions to the original, and after settling add gradually, and a very little at a time, some cyanide solution as long as a precipitate forms. Be careful not to add more than this. Allow the precipitate to settle thoroughly, pour off the liquid, and wash the residue by decantation several times. This gives us silver cyanide in nearly pure condition. Now dissolve 15 to 20 Gm. of commercial potassium cyanide in 200 Cc. of water and add this to the moist silver cyanide in a beaker or bottle. The latter goes into solution, forming the desired double cyanide with an excess of potassium cyanide left. Finally, dilute the whole with water to make a liter.

The articles to be plated are hung from copper wires in this bath and attached to the zinc pole of a battery of Bunsen or chromate cells. The current is led into the solution from the other pole through a plate of metallic silver. By this arrangement silver dissolves from the plate as fast as it is deposited on the article, thus keeping the solution of nearly constant strength. To insure an even deposit the article must be moved frequently to bring all sides, in turn, near the silver electrode.

The deposit thus formed has a rough or "matt" surface and can be given the usual smooth finish by rubbing with chalk or other polishing powder. On removing the plated article from the bath it is washed thoroughly in clean water and dried in an atmosphere free from tarnishing gases.

Compounds of Silver. Numerous compounds of this metal are known, but the most important are the nitrate, $AgNO_3$, the chloride, AgCl, the bromide, AgBr, and the iodide, AgI.

Silver Nitrate. This salt is made in large quantities by dissolving the metal in nitric acid. It is very soluble in water and is obtained crystallized in plates. The important uses of the nitrate are in the preparation of plating solutions, as just described, and in making certain salts employed in photography; under the name of *lunar caustic* it is also used in medicine. It is readily obtained in a state of great purity.

Silver Chloride, Bromide and Iodide. These three substances are interesting mainly because of their behavior in light. On this behavior the ordinary processes of photography are founded. Some experiments will be given illustrating these points.

Experiment 161. In each of three test-tubes take about 5 Cc. of a dilute solution of silver nitrate. Add to one a few Cc. of a solution of sodium chloride, to the second a solution of sodium bromide and to the third some dilute potassium iodide solution. In each case a curdy precipitate forms which is most characteristic after shaking. These precipitates are the chloride, the bromide and the iodide of silver, of which the first is white and the others yellowish white in dilute mixture. Divide the contents of each test-tube into three parts. To one part, in each case, add ammonia water. The precipitates of silver chloride and bromide dissolve while the iodide is found to be insoluble. It will be noticed that the chloride is much more easily soluble than the bromide. To another portion, from each one of the precipitated mixtures, add some solution of sodium thiosulphate. The three precipitates dissolve. Next, stand the remaining portions in bright sunlight. After a time it will be noticed that they darken and become violet in shade. The extent of this darkening can be materially increased by having a slight excess of silver nitrate present in each case, that is, a little more than can be precipitated by the salts added. After the three tubes have stood in the light long enough for their contents to darken throughout, which is aided by shaking occasionally, repeat the experiment of adding sodium thiosulphate. It will now be found that the precipitates have become insoluble. The action of the light has converted them into compounds which can no longer dissolve in a liquid which was a good solvent for the fresh precipitates.

The precipitations follow according to these equations:

$$AgNO_3 + NaCl = AgCl + NaNO_3$$
$$AgNO_3 + NaBr = AgBr + NaNO_3$$
$$AgNO_3 + KI = AgI + KNO_3$$

The experiment shows that in fresh condition these precipitates are soluble in a certain solution, that they are changed in some manner by exposure to light, and that after this change has taken place they are no longer soluble in the solution used. How this fact can be practically applied will be shown below. We need for the purpose what is called sensitive paper, that is, paper which holds on one surface a precipitate as above described. Such a paper may be prepared as follows:

Silver Paper.

Dissolve a gram of ammonium chloride in 15 Cc. of water and add about 1 Cc. of alcohol. To this solution add 50 Cc. of

strong white of egg solution. The white of egg for the purpose is best made by separating the yolk mechanically, and shaking the white portion thoroughly with broken glass and some water in a bottle. The mixture is allowed to settle, and then the liquid portion is filtered through well washed cotton into the other solution, as mentioned. The mixture is shaken and poured out into a shallow dish. On this liquid sheets of pure white slightly glazed paper, free from chemical bleaching agents, are floated a few minutes, and then hung up to drain and dry. The paper so prepared is next floated on a solution containing 10 Gm. of silver nitrate in 100 Cc. of water. This must be done in a darkened room. The paper is left on the solution three to five minutes. A precipitate of silver chloride in presence of an excess of silver nitrate forms. The paper so impregnated is hung up again in a dark room to drain and become dry. It is then kept in a box away from the light until used. The student may employ such paper, but it will generally be found more convenient to purchase similar paper from dealers in photographic supplies. With such paper the following simple experiment may be made:

Photography. Silver Printing.

Experiment 162. Cut out a small figure of any shape from a piece of dark paper and spread this over the center of a slightly larger piece of the above sensitive paper, and on the side holding the precipitate. Then place these between two pieces of clean, colorless glass, which may be clamped together at opposite corners by means of bits of brass wire. Expose the paper so held to the action of sunlight, the sensitive surface facing the light. The glass over the other surface should be covered by some opaque object to prevent the light from reaching the paper from this direction. After an exposure of ten minutes remove the glass in a part of the room away from bright light and observe that a white image of the object, represented by the cut opaque paper, is found on a dark ground. Wash the paper a minute in clean water and then immerse it for twenty minutes, with frequent stirring, in a solution containing 10 Gm. of sodium thiosulphate in 100 Cc. of water. After this treatment transfer the paper to clean water and allow it to soak an hour, with frequent changes of the water. Then hang it up or put it between blotting paper to dry. We have now a permanent silver print which may be exposed to the light without further change.

Next, repeat the above experiment, but do not wash the print in water or the sodium thiosulphate solution. It will be found that the print thus made is not permanent, even in a faint light. After a few days the light part will grow dark and in time the whole surface will be uniform in color, with complete loss of the image. Pieces of paper 5 Cm. square are large enough for the purpose.

The operations described above represent those carried out in

printing and fixing (making permanent) a photograph on paper. In practical work the sensitive paper is exposed behind a glass "negative," that is, a picture in light and shade, on glass, made by a process which cannot be well illustrated in all details in the ordinary laboratory. It may be said, however, of this process that the main chemical principles involved are the same as in printing and fixing the photograph.

Glass Negatives.

As employed in ordinary dry-plate photography, the negative plate is usually a sheet of glass on which the sensitive silver compound is held in the condition of a fine emulsion. Such an emulsion may be prepared by soaking gelatin in water to soften it, and then heating the mixture until homogeneous. To this, potassium bromide in solution is added and thoroughly distributed by stirring. Then a certain weight of silver nitrate in solution is poured in and thoroughly stirred to give a precipitate of silver bromide, which is very fine and evenly distributed through the whole mass. This is allowed to set and is then cut into thin strips, which are soaked in water until all excess of soluble bromide is washed out. What is left is softened in pure water, by aid of heat, and in this condition poured over clean glass plates, which are then allowed to stand on a level shelf in a place free from dust until the gelatin sets again. All of these operations must be performed in a nearly dark room, illuminated by faint nonactinic light only. The plates are afterward dried by warm air, after most of the moisture has evaporated at a low temperature.

Such plates when properly made are very sensitive, and may be kept indefinitely in the dark. When exposed in the camera the sensitive silver bromide is acted on by the light reflected from white or colored objects. The extent of the decomposition of the bromide is proportional to the intensity of the light reaching the plate through the lens of the camera; but when the plate is taken from its holder, in the dark room, and examined by a faint red light no change can be seen on it. It contains the elements of an image, but this is in a latent condition, and must be brought out by the aid of what is called a *developer*. This is a solution of some reducing or oxygen-absorbing substance, such as hydroquinone, ferrous sulphate, pyrogallol (called pyrogallic acid) and other bodies, dissolved with alkalies and certain additions which need not be mentioned here. On immersing the plate in the developing solution an image soon becomes visible, and this is formed by the precipitation of metallic silver as a film of greater or less thickness, producing variations in light and shade which may be compared to the heavy and light crayon strokes, properly applied, that are sufficient to make an image on a piece of white paper.

Wherever the light has acted strongly on the plate the development produces a relatively heavy precipitate of silver. Where

the light has been thrown with less intensity the silver deposit has less depth. We are not able to explain the exact nature of the change which the light brings about in the silver bromide on the plate, but it is certainly left in a condition in which reduction to the state of metal is relatively rapid. The reduction of the ordinary bromide, AgBr, is much slower. The action of the hydroquinone developer is illustrated by this equation:

$$2AgBr + C_6H_4O_2H_2 + 2KOH = 2Ag + 2KBr + 2H_2O + C_6H_4O_2$$

Hydroquinone, $C_6H_4O_2H_2$, in reducing the silver salt becomes oxidized to quinone, $C_6H_4O_2$. Addition of alkali to the developer hastens the action, and addition of bromide retards it, as it is a product of the reaction.

The photographer allows the plate to remain in the developing solution long enough to produce a good image, which is determined by frequent examination by aid of a faint red light. The plate is then washed in water a short time, and immersed next in the solution of sodium thiosulphate, as already described. This removes the silver salt present which is in excess of the amount needed to make the picture. Finally, the negative is thoroughly washed in water, and then stood on its edge to drain and become dry. It is after this ready for use to make "prints" or paper copies, as already illustrated. The sensitive paper and the glass negative are placed face to face in a printing frame, which is then exposed so that light may shine through the plain glass surface toward the paper. The dark parts of the negative, however, will not allow light to pass, and consequently the paper remains unacted upon at such points. On the other hand, it is strongly attacked where the silver deposit on the negative is thin, and an image is thus made on the paper corresponding to that on the glass, but with the lights and shades reversed. Light objects, therefore, which appear dark in the "negative" are properly represented in the print or "positive" picture.

The action of the sodium thiosulphate as a fixing agent depends on the fact that it dissolves silver bromide, or chloride, forming a soluble double salt.

$$Na_2S_2O_3 + AgBr = AgNaS_2O_3 + NaBr$$

Only the excess of bromide is removed in this manner. By sufficient washing the $AgNaS_2O_3$ may be wholly eliminated.

Other Silver Compounds. The most important of the silver compounds have been described in the foregoing, but a few others have special applications. Among other silver compounds there may be mentioned the oxide, Ag_2O, which with water behaves as an alkali, AgOH; the phosphate, Ag_3PO_4, a yellow precipitate; the chro-

mate, Ag_2CrO_4, a red precipitate, and the thiocyanate, AgSCN, a white precipitate, all of interest in analytical chemistry.

Recognition. Silver compounds are recognized by the formation of the precipitates just mentioned, and commonly by the precipitation of silver chloride on addition of hydrochloric acid to a silver solution. This precipitate dissolves in ammonia, in potassium cyanide solution, and in a thiosulphate solution.

GOLD.

Occurrence. The metal is usually found in the native condition disseminated through sand or quartz rocks or with pyrites. It may occur in the old eruptive rocks or veins, or in the disintegration products of such rocks, that is in sands or conglomerate masses. The chief gold producing countries are the United States, Dutch and British South Africa, Australia, Russia and British North America. In 1903 the world's production of gold was 491,553 kilograms, of which this country furnished 110,727 kilograms, or over one fifth. Australia furnished 131,613 kilograms.

History. We find gold mentioned in the earliest historical accounts, and it has always ranked as a standard of value. The gold known to the ancients was usually obtained by the washing of gold-bearing sands from the beds of rivers. The methods of separating it from rock masses are comparatively recent.

Metallurgy. Much that was said about silver applies to gold. When gold-bearing sands are shaken in an iron pan under a stream of water the lighter earthy particles are washed away and the heavy gold remains. In a modification of this process great banks of sand are washed down into long sluice boxes lined with amalgamated copper sheets. The heavy gold lags behind, much of it being held by the mercury, while the lighter sands are gradually carried away by the running water in the sluices, which may be hundreds of feet in length. The gold is scraped up from the bottom of the boxes and refined. Where gold occurs in masses of solid rock such processes will not suffice and it is necessary to resort to others.

Amalgamation Process. In this the rock is crushed and ground to a fine powder in stamp mills. It is washed from under the stamps by a stream of running water into large vats

where it is agitated with mercury, which gathers up the gold particles from the mud and dissolves them as in the case of silver. This amalgam is afterwards collected and distilled, the mercury being saved and the gold left in impure condition. It is then melted into bars and sent to the refiner.

Smelting Process. Many ores cannot be economically or completely extracted by the mercury method and these are often treated by smelting with lead ores, exactly as described for silver. The treatment of the base bullion obtained is the same as there given. At the present time a large part of the rich ore in this country is so handled.

Cyanide Process. Metallic gold is dissolved by solutions of potassium cyanide under certain conditions, and a process suggested years ago has recently been revived by which many of the poorer gold ores are successfully treated in great quantities. The ores are crushed, sometimes after preliminary roasting, and percolated in tanks with a weak solution of potassium cyanide to which sodium dioxide is sometimes added to hasten oxidation. The reactions taking place are somewhat complex, but the most probable ones are these:

$$2Au + 4KCN + H_2O + O = 2AuK(CN)_2 + 2KOH$$
$$Au + 2KCN + H_2O = AuK(CN)_2 + KOH + H$$

Silver in the ores dissolves in the same manner. By this solvent action it is possible to dissolve traces of the precious metals from large quantities of sand or crushed rock. From the solutions obtained the gold and silver are precipitated by electricity or by addition of metallic zinc:

$$2KAu(CN)_2 + Zn = K_2Zn(CN)_4 + 2Au$$

The gold settles to the bottom of the precipitation tanks as a fine slime. It is collected, dried, smelted and refined.

Chlorination and Bromination Processes. In these the ores are roasted to destroy sulphides and then subjected in casks to the action of chlorine gas or bromine vapor. The gold dissolves to form the chloride, $AuCl_3$, or bromide, which is readily soluble in water. At the end of the treatment water is allowed to percolate through the casks to wash out the soluble salt. From this solution the gold is precipitated by charcoal powder or by ferrous sulphate:

$$AuCl_3 + 3FeSO_4 = Au + Fe_2(SO_4)_3 + FeCl_3$$

The gold settles out as a fine, dark powder, which is collected, dried and refined.

Refining of Gold. The crude gold bullion obtained by any one of the above processes contains silver usually, and possibly small amounts of copper and other metals;

it must therefore be subjected to a separating or refining process. For many years the following method was commonly followed, and is yet to some extent. The metal is assayed and, if rich in gold, enough silver is melted in with it to make the gold about one fourth of the whole. Such an alloy is readily attacked by nitric acid, while in alloys much richer in gold the action is very slow or may not take place at all. In the weak alloy all the baser metals are easily dissolved as nitrates, while the gold is left as a dark, spongy mass, which may be washed quite pure with water. After this treatment it is dried and melted into bars of fine gold. The mixed nitrate solution and washings is precipitated with common salt, which throws down, as chlorides, all the silver and some of the lead which may be present in the gold of certain processes. But lead chloride is easily soluble in hot water and is so washed out, leaving pure silver chloride. When this is sufficiently washed it is dried and melted with dry sodium carbonate, which decomposes the chloride, leaving pure metallic silver ready for casting in bars.

Another method very commonly employed now is parting with sulphuric acid, and this method is usually followed in separating the silver and gold in the cupelled metal, described under silver. This silver-gold alloy is boiled up in iron kettles with strong sulphuric acid, which dissolves the silver and traces of other metals as sulphates, leaving the gold as a brown, spongy mass. This is separated by straining, washed thoroughly with water, dried and melted in a crucible with sodium carbonate and charcoal, which leaves it practically chemically pure. The solution of silver sulphate is run into copper lined tanks, in which are suspended sheets of copper. This metal displaces the silver, which precipitates as a fine powder, leaving copper sulphate as the by-product in solution. The fine silver is collected from the bottom of the tanks, thoroughly washed, and pressed dry, and then fused with sodium carbonate and a little charcoal, yielding a product of a high degree of purity. The copper sulphate is recovered by crystallization.

Properties. Gold is the most malleable and ductile of

metals. It may be beaten into foil so thin that light passes through it. Gold alloys with many heavy metals readily, as already shown. It does not dissolve in any one of the common acids, but rather readily in aqua regia.

Uses. The uses of the metal are numerous and important. It constitutes the standard coinage of most nations, for this purpose being alloyed usually with copper. The coinage of the United States and France consists of 90 parts of gold to 10 of copper; that of Great Britain is a little richer in gold, 91.666 per cent. For articles of jewelry and ornamentation the amount of gold varies between 40 and 75 per cent, the fineness being usually expressed in carats. Pure gold is said to be 24 carats fine; 18 carat gold contains 18 parts in 24, or 75 per cent of pure gold and 25 per cent of alloy. It is necessary to make these additions to gold, as alone it is too soft for ordinary uses. Fourteen carat gold preserves its bright color even in the worst laboratory atmosphere, and is commonly used in making rings, watch chains and cases. Because of its great malleability gold is largely used by dentists in the filling of teeth, and is commonly employed in the condition of thin leaf or foil. This leaf is also used in the lettering of books and ornamentation of leather for many purposes. Gold is readily deposited as a plate from a cyanide bath as described under silver, and this application is an extended one.

Compounds of Gold. The compounds of gold are much less numerous than are those of most of the other metals. Among the soluble salts the chloride, $AuCl_3$, is the most important. It is employed by photographers in a toning solution. This chloride combines with the alkali chlorides, forming crystalline double salts.

Recognition. Compounds of gold are easily recognized by the dark brown precipitate which their solutions yield when treated with a solution of ferrous sulphate, also by the formation of a deep purple color obtained by adding to a gold solution a mixture of stannous and stannic chlorides. This color is known as the purple of Cassius.

CHAPTER XVI.

THE ALKALI-EARTH GROUP: GLUCINUM, MAGNESIUM, CALCIUM, STRONTIUM AND BARIUM.—THE SPECTROSCOPE.

GENERAL CHARACTERISTICS.

We have here a group of five members in which certain marked resemblances are easily seen. In their physical behavior the metals are much alike, with a gradual change of properties, however, from the lightest, glucinum, to the heaviest, barium. In their compounds they commonly act as bivalent, forming oxides, MO, and hydroxides, MO_2H_2. The hydroxides behave as strong bases. The phosphates and carbonates are insoluble in water, in which respect they differ from the alkalies and resemble the heavier metals. The sulphates of glucinum and magnesium are soluble in water, resembling zinc sulphate, while the sulphates of calcium, strontium and barium are characterized by their very slight solubility. The pronounced basic character of the members of this group increases with the atomic weight. Glucinum does not decompose water at any temperature, magnesium acts slowly on hot water, while barium behaves as energetically as sodium and potassium. Glucinum and magnesium hydroxides are practically insoluble in water and both decompose at comparatively low temperatures, leaving oxides; the other hydroxides are more soluble and more stable; in fact, barium hydroxide can be fused like KOH or $NaOH$, and it is soluble enough to form a strongly alkaline solution. The following table shows the range of atomic volumes and other properties:

	Atomic Weight.	Specific Gravity.	Atomic Volume.	Melting Point.	Boiling Point.
Glucinum	9.1	1.64	5.5	940°	.....
Magnesium	24.36	1.75	13.9	750°	1100°
Calcium	40.1	1.58	25.4	760°	.....
Strontium	87.6	2.54	34.5	Red heat.	.....
Barium	137.4	3.75	36.6	1150°	.....

The melting and boiling points in this group have not been very accurately determined. The values given are probably close approximations, but here, as in the alkali group, we notice an increase in atomic volume and relative decrease in melting point with an increase in the atomic weight, conditions which must have some intimate connection with the nature of the atoms themselves.

GLUCINUM.

Occurrence. This metal is found in a number of comparatively rare minerals, of which the most important are beryl and emerald, which are essentially $Be_3Al_2(SiO_3)_6$, and chrysoberyl, $BeAl_2O_4$. The term *emerald* is applied to transparent beryls with a green tinge, while if they have a blue color they are called *aquamarins.*

History. The oxide was recognized in 1797 and the metal was isolated in 1828 by fusion of the chloride with metallic potassium. It has been isolated by several other processes since, and has been found to be somewhat malleable and capable of taking a polish.

Compounds of Glucinum. These are of little importance. The salts are mostly soluble in water and possess a bitter sweetish taste, by which they may be recognized. The chloride and sulphate are easily obtained in crystalline condition. On account of the sweetish taste the name glucinum is given to the metal. It is also known as beryllium. The metal and the salts are without technical importance.

MAGNESIUM.

Occurrence. It is found in a large number of minerals and very widely distributed. The best known are the

carbonate or magnesite, $MgCO_3$, dolomite, $MgCO_3.CaCO_3$, kieserite, $MgSO_4.H_2O$, carnallite, $MgCl_2.KCl.6H_2O$, and several silicates. The sulphate and chloride are found in many mineral springs.

History. The sulphate was produced from the water of Epsom springs in the seventeenth century, and the oxide or *magnesia alba* obtained from it in 1707. As this substance was first made it was very impure and was for a long time confounded with lime, but Black showed the difference between them in 1755. Davy attempted to isolate the metal which he recognized the magnesia alba must contain, but was not able to secure it in pure form. This was accomplished by Bussy in 1830, who fused the dry chloride with potassium:

$$MgCl_2 + K_2 = Mg + 2KCl$$

Preparation. The method just mentioned served for the preparation of the metal for years. Bunsen showed in 1852 that it could be isolated by electrolysis of the fused chloride, and methods based on this behavior are in use on the large scale. A great deal of magnesium is made by fusing a mixture of the dry chloride with fluorspar and metallic sodium, the latter being cheaper than potassium. The reduced metal is now purified by distillation.

Properties. Magnesium is a white, malleable and ductile metal which may be drawn into wire when warm. It breaks with a crystalline fracture. When heated in the air to a high temperature it burns with an intense white light.

Experiment 163. Heat a short piece of magnesium wire in the flame of a Bunsen burner. When combustion begins remove it from the lamp and allow it to burn freely in the air. The light is often employed in photography.

Uses. As just suggested, in photography, as the light is strongly actinic. The powder, pure or mixed with potassium chlorate, or other substance, is generally used instead of the wire, because the combustion is more in-

tense. But these mixtures must be handled with care; spontaneous explosions have followed with them.

Magnesium Oxide. This substance, known also as *magnesia*, is the white powder which is formed when the metal is burned in air or in oxygen. Practically it is made by strongly heating the carbonate, which decomposes as follows:

$$MgCO_3 = MgO + CO_2$$

The oxide is practically insoluble in water. Magnesium hydroxide, MgO_2H_2, is formed by precipitating magnesium sulphate or chloride by sodium hydroxide, or by long contact of the oxide with water.

Magnesium Carbonate is found in nature in nearly pure condition and, mixed with calcium carbonate, as dolomite. An artificial product is easily made by precipitating the sulphate by sodium carbonate, but contains always some magnesium hydroxide, because of the effect of hydrolysis on the combination of the strong base and very weak acid. In presence of ammonium salts precipitation is very imperfect. Ammonium carbonate only partially precipitates magnesium salts. If the solution contains a sufficient amount of ammonium chloride no precipitate whatever forms, which is usually explained by assuming the formation of a soluble double salt.

What was said in an earlier chapter on the constancy of the solubility product offers another explanation of this phenomenon with the hydroxide. We have

$$\frac{C_{Mg} \times C^2_{(OH)}}{C_{MgO_2H_2}} = K$$

The addition of ammonium chloride, or other salt, would lead to the formation of the slightly dissociated ammonium hydroxide by aid of the numerator hydroxyl. More and more of the MgO_2H_2 would therefore have to dissolve to maintain the equilibrium, and such a precipitate, if once formed, would gradually disappear.

Experiment 164. Let the student prepare a solution of magnesium sulphate and divide it into several portions. To one add sodium carbonate, to another ammonium carbonate and to a third and fourth portions ammonium chloride solution and then these carbonates. Observe the different behaviors.

The following equation represents the reaction between magnesium sulphate and sodium carbonate:

$$5MgSO_4 + 5Na_2CO_3 + 6H_2O = 5Na_2SO_4 + 4MgCO_3.MgO_2H_2.5H_2O + CO_2$$

The composition of the precipitate varies with the concentration and temperature of the solutions.

Magnesium Chloride is a soluble crystalline salt obtained by dissolving the carbonate in hydrochloric acid. It is used in analytical chemistry.

Magnesium Sulphate. This salt has been already referred to. It is made by purifying the native mineral or by the action of sulphuric acid on dolomite. The sulphates of magnesium and calcium are formed, but the latter is so slightly soluble in water that a separation is easily made, permitting the magnesium compound to be obtained in practically pure condition. It has many uses, and is the starting point in the manufacture of other compounds of the metal. As commonly met with in commerce it is in the crystalline condition known as Epsom salt, $MgSO_4.7H_2O$. It will be seen later that we have here the first one of an important group of sulphates which crystallize with 7 molecules of water and which are isomorphous and similar in many respects.

Magnesium Phosphates. Several are known, distinguished by their insolubility. Ammonium magnesium phosphate, or triple phosphate, $NH_4MgPO_4.6H_2O$, is a characteristic crystalline precipitate.

Recognition. Magnesium compounds may be recognized by the formation of the precipitate just mentioned, obtained by adding sodium phosphate to a magnesium solution containing ammonium chloride and hydroxide.

CALCIUM.

Occurrence. The metal is found as carbonate in limestone, marble, chalk and coral; as a sulphate in gypsum and anhydrite; as phosphate in bone ash and in apatite; as silicate in many minerals and less abundantly in other combinations.

History and Preparation. Lime was known to the ancients, and until the beginning of last century was supposed to be a simple substance. Davy showed that this is the oxide of the metal which he succeeded in isolating by electrolysis of the chloride. By recently improved methods it may be separated in quantity and would be as cheap as sodium if there were corresponding demands for it.

Properties and Uses. Calcium as formerly made is a yellow metal much like brass in appearance, which oxidizes readily in moist air and decomposes water quickly. But the new electrolytic metal is as white as sodium. It may be preserved under benzine. When ignited it burns with a bright yellow light. Technical uses are yet to be discovered.

Calcium Oxide. This substance is known commonly as *lime*, having the formula CaO. It is made by strongly heating limestone or marble:

$$CaCO_3 = CaO + CO_2$$

This decomposition is usually carried out in lime kilns with the loss of the CO_2. But the reaction is really a reversible one, since lime absorbs carbon dioxide under other conditions. It should then be written:

$$CaCO_3 \rightleftarrows CaO + CO_2$$

Some interesting experiments have been carried out to determine the conditions of equilibrium in the reaction.

Calcium Hydroxide. This substance is known as slaked lime, and has the composition represented by the formula CaO_2H_2 or $Ca(OH)_2$.

Experiment 165. Put a piece of soft, well burned lime, as large as a walnut, in a porcelain dish, and pour over it some lukewarm water, a few drops at a time. The lime absorbs the water and soon begins to swell and then crumble. After the piece has become thoroughly disintegrated add enough water to make a thick liquid and stir well with a glass rod. The product is known as *milk of lime*. Pour a few drops into a test-tube and add some more water, and then phenol-phthalein. A red color is produced, showing that the substance is an alkali. Into another test-tube pour more of the milky liquid, add an equal volume of water and then filter through a small filter into a clean flask or beaker. Add phenol-phthalein to the filtrate. It is found to be alkaline. Then make some very dilute hydrochloric acid, by diluting the weakest laboratory acid with ten times the volume of water (1 Cc. with 10 of water will be enough), and pour a little of this into the colored filtrate. Notice that the color is soon discharged, showing that the amount of real alkali present must be very small. The slaked lime is only slightly soluble in water. Now divide what remains of the milk of lime into two portions; to one add strong hydrochloric acid and to the other add strong nitric acid. Clear, or nearly clear solutions are obtained, showing that the slaked lime, while but slightly soluble in water, is readily soluble in the two acids, but with formation of new substances.

The clear solution of the slaked lime in water is known as *lime-water*. About 700 parts of cold water are required to dissolve one part of the substance. It is much less soluble in hot water. The reaction which takes place in slaking the lime is represented by the equation:

$$CaO + H_2O = CaO_2H_2$$

With a moderate amount of water this slaked lime yields *milk of lime*, while in a great excess it is soluble, yielding *lime-water*. The behavior of the clear solution with carbonic acid gas from the air or from the lungs has been shown already. This lime-water is therefore a very useful test for CO_2, and is commonly used for the purpose.

Slaked lime is used mainly in making mortar, but also in great quantities in chemical industries, as illustrated in the liberation of ammonia.

Common mortar is a mixture of slaked lime and sand and hardens mainly through the absorption of carbon dioxide by the lime, thus forming carbonate.

Calcium Carbonate. As stated above, this occurs in nature in various forms, and may be produced by precipitating a solution of calcium chloride with one of ammonium or sodium carbonate. In this form it is a fine white powder and has several uses. Calcium carbonate is very nearly insoluble in pure water, but dissolves appreciably in water containing carbonic acid, with formation of bicarbonate:

$$CaCO_3 + CO_2 + H_2O = H_2Ca(CO_3)_2$$

The temporary hardness of most natural water is due to the presence of this and the analogous magnesium bicarbonate. Both compounds are destroyed by boiling the water.

Calcium Chloride. This salt is usually made by dissolving marble in hydrochloric acid. It comes into commerce as the anhydrous salt, $CaCl_2$, or a crystallized product, $CaCl_2.6H_2O$. A partially dried product with $2H_2O$ is obtained from the latter by heating to 200°, and is used often instead of the anhydrous salt in drying gases or organic liquids. Calcium chloride is a by-product in several chemical industries.

Calcium Sulphate. This important substance is represented by the formula $CaSO_4$. In nature it is found in large quantities as gypsum, $CaSO_4.2H_2O$. When a gentle heat is applied to the gypsum it loses its water of crystallization and forms the dry substance, or *plaster of Paris*. This plaster of Paris is distinguished by its property of hardening when mixed with a little water, and is therefore used as a cement, and as a substance for taking casts and making surgical dressings. The use in making casts or copies of coins and medals can be shown by the following experiment:

Experiment 166. Rub a little oil over a large coin or medal and then remove most of it with the finger, leaving enough, however, to form a very thin uniform layer over the metal surface. Then mix 15 or 20 Gm. of plaster of Paris with enough water to form a thick cream, and without delay, pour this over the coin

so as to form a layer half a centimeter or more in thickness. A strip of paper should be wrapped around the coin so as to form a cell into which the creamy mass is poured. In a few minutes the plaster "sets," but it should be allowed to remain long enough to become quite hard. The solid plaster cast can then be removed very easily and shows every feature of the coin in reversed position.

When gypsum is heated to a temperature of 200° it becomes *overburnt* and will no longer take up water readily.

Other Compounds. Several of these must be mentioned briefly. Calcium nitrate is found as a deposit in many caves and is called "cave niter." Calcium hypochlorite is the active constituent of bleaching powder and has the formula CaO_2Cl_2. It is made by passing chlorine gas over slaked lime. The bleaching powder of commerce is a mixture of the hypochlorite, with calcium chloride resulting in the reaction, and some unchanged lime. Calcium phosphate in crude form is found in bone ash from the burning of bones, also in large deposits in the earth, some of which have had their origin in the bones of animals. Calcium metaborate is an important mineral, and the source of much of the boric acid and borax of commerce. The carbide of calcium, CaC_2, is now an important substance produced by subjecting a mixture of coke and lime to the heat of the electric arc. With water it yields acetylene, already described.

Recognition. Calcium compounds are recognized by the reddish yellow color they impart to the flame of the Bunsen burner, by the bright red and bright green line they exhibit in the spectroscope, and by the white precipitates produced in their solutions when made alkaline and mixed with solutions of ammonium carbonate or oxalate. Precipitated calcium oxalate, $CaC_2O_4.2H_2O$, is a very insoluble substance.

STRONTIUM.

Occurrence. The metal is comparatively rare, being found in a few minerals only and these not abundant. The sulphate, celestine, $SrSO_4$, and the carbonate, strontianite, $SrCO_3$, are the most important.

History. The carbonate was first mistaken for barium carbonate, but in 1792 the distinction was shown. In 1808 Davy isolated the metal in impure condition by electrolysis of the chloride. It is still prepared in that way, but not easily, and is therefore rare as a metal.

Properties. It is a light metal which oxidizes very readily and decomposes water with great energy. It has no scientific or technical uses.

Compounds of Strontium. Of these the most important are the oxide, the chloride, the nitrate and the chlorate. The oxide yields the hydroxide, SrO_2H_2, which combines readily with sugar, forming a crystalline saccharate of some importance in sugar refining. The nitrate and chlorate are used mainly in fireworks mixtures, to which they impart a bright red color.

Recognition. Strontium compounds color the flame of the Bunsen burner bright red; they also show a number of characteristic red lines in the spectroscope. Solutions of strontium compounds yield a white precipitate of the carbonate when treated with ammonium carbonate.

BARIUM.

Occurrence. This element is found mainly in heavy spar, $BaSO_4$, and in the carbonate or witherite, $BaCO_3$, the first of which is a comparatively common mineral.

History and Preparation. Some of the properties of heavy spar have been known since early in the seventeenth century. Scheele, in 1774, showed that it contained a new earth and Davy showed that this earth is the oxide of the metal now called barium. His attempts at isolating the metal in pure condition were not successful; Bunsen and others later succeeded in obtaining it by electrolysis, but the process is a difficult one.

Properties. The metal appears to be silver white like the recently prepared calcium and strontium; but it oxidizes with extreme readiness, so that it is possible that a pure substance has never been secured. Authori-

ties differ as to the melting point of the metal. By some it is placed higher than that of cast iron, while by others it is given as lower than that of strontium. The metal has no uses in the arts.

Barium Oxide, BaO, is obtained by ignition of the nitrate or carbonate at a high temperature. To reduce the carbonate in quantity it is best to add carbon to it. The pure oxide is a heavy white powder, which when heated in the air or oxygen to redness absorbs a second atom of oxygen with formation of the dioxide, BaO_2. This second atom is given off at a bright red heat and on this behavior is founded a method of preparing oxygen from the air in quantity. The dioxide is used, as already illustrated, in the production of hydrogen dioxide.

Barium Hydroxide. The oxide, BaO, combines very readily with water forming BaO_2H_2, which dissolves in considerable quantity and forms a crystalline product, $BaO_2H_2.8H_2O$. This is a valuable reagent because of its strong alkaline reaction and power of absorbing CO_2. It is also used in the separation of sugar from solutions.

Barium Chloride. This salt is prepared by dissolving barium carbonate in hydrochloric acid. It is readily soluble in water, from which it crystallizes as $BaCl_2.2H_2O$. A solution of this salt is a valuable reagent for the precipitation of sulphates.

Other Compounds. The nitrate, $Ba(NO_3)_2$, and the chlorate, $Ba(ClO_3)_2$, are used in fireworks to impart a greenish yellow color. The sulphate, in the form of ground heavy spar, is very commonly used as an adulterant in white lead paints. It has less value as a pigment itself.

Recognition. Barium compounds color the Bunsen flame greenish yellow, and in the spectroscope show a number of yellow and green lines. Sulphates produce in barium solutions a heavy white precipitate of barium sulphate, which is extremely insoluble in water and acids.

THE USE OF THE SPECTROSCOPE.

It has been shown already that several metals may be detected by the colors which their salts impart to the flame of the Bunsen burner, in which they are heated on a platinum wire. When a clean platinum wire is dipped in a strong solution of the chloride or nitrate of calcium, barium, strontium, sodium, potassium or lithium and then held in a Bunsen flame a characteristic color is produced which is sufficient for the immediate identification of the metal, as long as one only is present. Suppose, however, that we have a potassium salt mixed with an equal or greater quantity of a salt of lithium, sodium, calcium or strontium. It will be found now on making the test that the potassium color is wholly obscured or uncertain. In the same manner it may be shown that a small amount of a calcium salt may be hidden by strontium, sodium, or barium even. The application of these flame tests to mixtures may lead, therefore, to quite imperfect conclusions, because the eye is not able to recognize certain colors in presence of others.

Now, the flame appears colored by the volatilization of these salts, because at a high temperature they are decomposed and the products of decomposition thrown into very rapid rates of vibration. These different rates of vibration are in turn communicated to the surrounding ether, and this is the medium which brings the impression to the eye. What is called light is, outside the body, a rate of motion. Different rates of ether motion conveyed through the transparent media of the eye to the retina produce there different impressions, which, communicated by the optic nerve to the brain, give to the individual the sensations of different kinds of light. These sensations are commonly resultant effects produced by the blending of different simultaneous disturbances of the same part of the retina.

Suppose, however, that the light from the colored flame can reach the eye only after passing through a colorless transparent prism, of glass preferably. Two new phenomena are immediately noticed. The light is deviated or bent from its direct course; that is, it has suffered

refraction, and it has also been *dispersed* or broken up into lights of various shades. This is due to the fact that the different ethereal disturbances are conveyed through the substance of the glass with different degrees of facility. The light motions in some cases are more retarded than in others, and hence the separation of the component parts of what is termed the beam of light after it leaves the prism. The eye brought opposite different points of the prism, in the same plane perpendicular to the refractive surfaces of the prism, receives now separate and distinct sensations as it would from several colored lights burning near together, one blue, one red, one green, and so on.

The images reaching the eye are rendered sharper and more clearly distinguishable if a very narrow vertical slit is placed in front of the prism, and if between the latter and the eye we have a double convex lens or small tele-

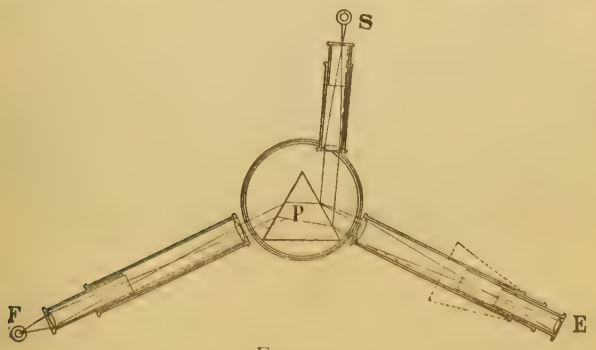

FIG. 27.

scope to take up the rays and throw them into the eye in nearly parallel direction. Such an arrangement would constitute, in fact, a simple *spectroscope*, and is shown diagrammatically in Fig. 27.

The actual arrangement of a spectroscope is shown in Fig. 28.

The optical parts of the instrument are supported on the base, F. The prism, P, has a refractive angle of 60°,

usually. B is a tube furnished with lenses and constitutes an observing telescope. C is the *collimator* tube which receives and renders parallel the rays of light coming to the prism from the flame or other object under examination. It has a double convex lens in the end near the prism, and at the other end is the slit, which can be adjusted so as to be exactly in the focus of the lens. By this arrangement the light rays thrown on the prism are

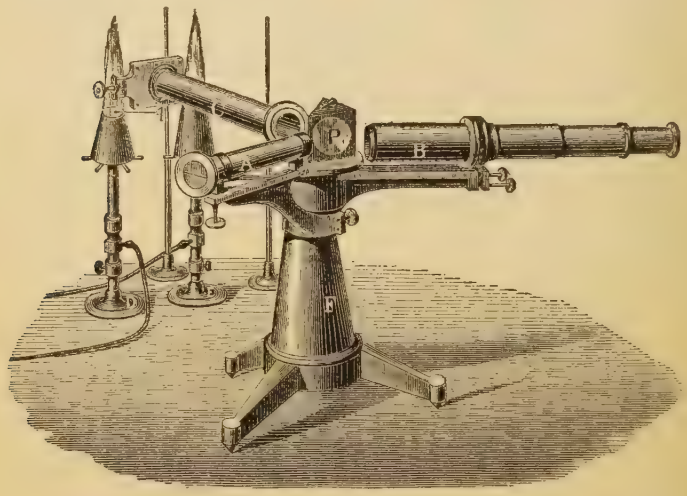

Fig. 28.

made nearly parallel. The tube A carries at its outer end a fine scale photographed on glass. This can be illuminated by a lamp and its image so thrown on the surface of P as to be reflected into the telescope, B. The lines on this scale serve to designate, arbitrarily, the position of the colored bands or lines of the spectrum produced and seen at the same time.

In Fig. 29 we have an illustration of the slit through which the light enters the instrument.

This slit must always be very narrow, but its width may be varied by the screw shown at the right. The lower

half of the slit is covered with a small prism. Light enters the upper part of the slit from directly in front,

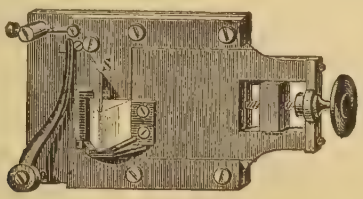

Fig. 29.

while by reflection from one of the surfaces of the small prism it may be made to enter the lower part of the slit from the side. By this arrangement it is possible to compare two different lights and obtain two different spectra, one above the other. In the illustration the lamp D is in front of the slit, while E is at one side and furnishes light to the prism P by reflection from the small prism on the slit front.

The working of the apparatus as a whole may now be illustrated. If we place in front of the open slit an ordinary illuminating gas burner, or if we throw sunlight directly into it, the eye at the end of B receives the ordinary *solar* or *continuous* spectrum. If, however, a Bunsen burner be placed in front, and in this a little sodium chloride be volatilized, the eye perceives now a single bright yellow band, which is merely the image of the slit, and varies in width with the width of the latter. If calcium chloride be volatilized in the flame several lines will be seen, two of which, a bright green and a bright red, are prominent. A salt of strontium yields a number of bright lines, mostly red. Further examination will show that the results, as far as the positions of the lines are concerned, are the same whatever salts of the metals we use and whatever the temperature, within rather wide limits. Our ordinary spectrum analysis is based on these facts.

By use of the illuminated scale we may note the relative positions of all these lines, and make a chart of them

such as is shown in the figure below. The color of the lines is shown by the colors of the solar spectrum desig-

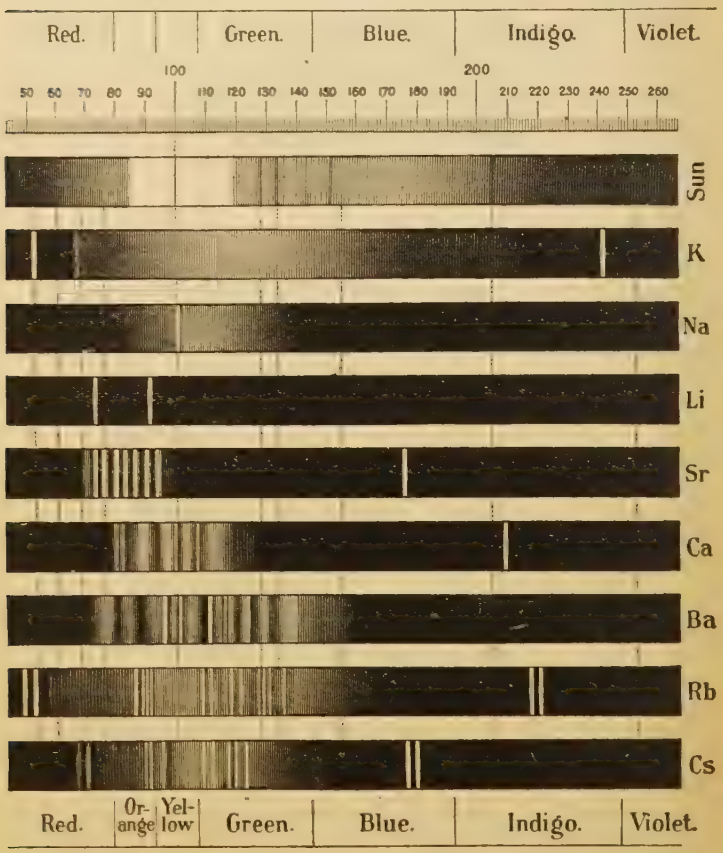

FIG. 30.

Showing the number and positions of the important lines in the spectra of some of the metals.

nated in the upper portion of the figure. The positions of the lines vary on the scale with the nature of the prism.

Hence, a chart made in this manner can show the results obtained in a particular instrument only.

Observations are best made in a dark room, the light entering the apparatus from the flame under examination only. But for the ordinary purposes very good results can be secured by mounting the spectroscope in a dark corner of a laboratory, protected from acid and hydrogen sulphide fumes. The prism should be covered with a dark paper cap, with openings opposite the tubes only.

While all salts of a metal yield the same bands at a temperature sufficiently elevated, for practical purposes it is best to work with those easily volatilized, as the chlorides or nitrates. The intensity of the spectrum is usually increased by moistening the substance under examination with hydrochloric acid. Some of the semi-solid mixture or strong solution is taken up on the loop of a platinum wire and held in the flame, as shown in the illustration.

With a little practice the student can make himself thoroughly familiar with the number and position of the lines given by the different metals. With these in mind he is able to control, to some extent, the results of his analyses by precipitation and to detect the presence of several elements briefly discussed in the preceding pages. Lithium, for example, is a constituent of many natural waters and it can be most readily found by concentrating the water to a small volume and applying the test to the residue. For small traces of lithium, with large quantities of other salts, the latter must be removed by precipitation before making the actual test, as will be suggested below. By the aid of the spectroscope several metals have been discovered. Of these may be mentioned cæsium and rubidium, by Bunsen and Kirchhoff; thallium, by Crookes; and gallium, by Lecoq de Boisbaudran. As an illustration of the detection of lithium, let the student evaporate several hundred cubic centimeters of artesian water to dryness in a porcelain dish. To the evaporating solution add a *few drops* of solution of pure potassium carbonate. Heat the residue strongly, allow it to cool and then add a few Cc. of distilled water, boil and filter.

Wash the residue with 1 Cc. of boiling water and add this filtrate to the other. By this treatment much of the calcium, barium, strontium, magnesium, iron and other metals possibly present is separated. Next evaporate the filtrate nearly to dryness, after adding enough hydrochloric acid to change the reaction. Mix the residue with strong alcohol, using a few Cc. only. Stir and filter. Lithium chloride, being soluble in alcohol, is separated in this manner from the bulk of the other alkali chlorides. Evaporate the alcohol filtrate and test the residue with the spectroscope. A single bright red line is characteristic of lithium, but in this and nearly all other tests the yellow line of sodium will be seen because of the practical difficulty of separating traces of this metal from substances under examination, and because, further, of the very great delicacy of the sodium reaction, a minute trace being sufficient to show a sharp line.

Absorption Spectra.

To illustrate another very important branch of spectrum analysis let the student prepare very dilute solutions of potassium dichromate, potassium permanganate, aniline red and other substances which yield colored solutions. Pour these in test-tubes, which support between the slit of the spectroscope and a luminous gas or oil lamp flame. It will be observed that a part only of the continuous spectrum is now visible, some of the colors being absorbed by the solutions in the tubes. The position and number of these zones or bands of absorption are characteristic for solutions of many colored substances. Applications of these principles are found mainly in the examination of organic coloring matters.

Direct Vision Spectroscopes.

For many purposes much simpler apparatus than described may be employed in the examination of metallic spectra. The *direct vision spectroscope* is an instrument illustrated in the next figure in which the flame, slit, prisms and eye are in one straight line. The dimensions of the

apparatus may be thus much reduced. By a combination of small prisms, mounted in a brass tube, it is possible to correct the refraction, without eliminating their dispersion effect. Direct vision spectroscopes are usually

FIG. 31.

made small and are employed for special purposes only. But occasionally they are made with large prisms for more elaborate investigations. In Fig. 31 the light enters through A and emerges at C.

CHAPTER XVII.

ZINC, CADMIUM AND MERCURY.

GENERAL CHARACTERISTICS.

These elements bear the same relation to the alkali-earth metals that copper, silver and gold bear to the true alkali metals. In all of their important compounds zinc and cadmium are bivalent, while mercury forms two series of compounds, the mercurous and mercuric. The latter are the most common and stable. The table below exhibits the important physical characteristics of the three metals.

	Atomic Weight.	Specific Gravity	Atomic Volume.	Melting Point.	Boiling Point.	Vapor Density. H=1
Zinc	65.4	7.15	9.16	420°	930°	33.9
Cadmium	112.4	8.65	12.99	320	770	56.0
Mercury	200.0	13.59	14.71	— 39	357	100.3

It will be observed that here, as before, we have a decrease in the melting and boiling points corresponding to an increase in the atomic weight. The vapor densities of these metals have been determined with considerable accuracy, and it follows from the results found that the atomic and molecular weights are the same: that is, the molecule of each in the state of vapor contains but one atom.

ZINC.

Occurrence. The metal occurs in many parts of the world as blende, ZnS, calamine, $ZnCO_3$, siliceous calamine, $Zn_2SiO_4.H_2O$, franklinite, an oxide of zinc, iron and manganese, and in other ores. The first is the most important.

History. Zinc was not known in pure condition to the ancients, although brass, its alloy with copper, was. This was made by smelting copper with certain ores, the composition of which was not understood. In the sixteenth and seventeenth centuries several writers mention zinc, but how it was obtained or from what ores is not now apparent. It seems to be certain that the metal was first separated in quantity in England about 1730, but the process was kept a secret for many years. In 1709 works were established in Germany and later elsewhere.

Metallurgy. The metal is always reduced from the oxide, the common sulphide being first brought into that condition by roasting in a current of air. The oxide is packed into small retorts with fine coal and subjected to distillation, a large number of these retorts being heated at one time in a furnace. At a high heat this reaction follows:

$$ZnO + C = Zn + CO$$

The temperature required for this reaction is so high that the liberated metal distills from the retorts into small receivers attached, where it condenses.

Zinc is produced mainly in the United States, France, Belgium, Germany and Great Britain. The world's production for 1903 was 571,705 metric tons, of which this country furnished 141,792 metric tons, Belgium furnished 155,297 and Germany 182,548 metric tons.

Properties. Zinc is a light colored metal with a peculiar bluish tinge. In thick pieces it is brittle at the ordinary temperature. Above 100° it becomes readily malleable, and at 130° it may be rolled out into sheets. At 200° it becomes brittle again and may be powdered in a mortar. The melting and boiling temperatures are given in a table above. It is acted on but slightly by dry or moist air, but dissolves easily in acids, and also in strong alkali solutions. With the last it forms zincates.

Uses. Zinc is largely used in sheet form for roofing and manufacture of many articles. As a coating on iron

it forms *galvanized* iron. With copper it yields several alloys, brass being the best known. In galvanic batteries it is usually the active element, and for this purpose large quantities are consumed. It is employed in the precipitation of certain metals, less basic in their character, as illustrated by this experiment:

Experiment 167. Pour a dilute solution of copper sulphate into a beaker, and add to it some small fragments of zinc. In a short time the zinc becomes covered with a spongy coating of copper. If time enough be given all of the copper will disappear from the solution, as shown by loss of color, a corresponding amount of zinc taking its place, as indicated by this reaction:

$$Zn + CuSO_4 = ZnSO_4 + Cu$$

A somewhat similar behavior with lead will be later illustrated.

Zinc Oxide. This substance is known as zinc white and is made in large quantities by direct oxidation of zinc in a current of air. It is used as a pigment because of its permanent white color even in atmospheres containing traces of hydrogen sulphide. When heated the oxide becomes yellow, but on cooling it returns to white.

Zinc Hydroxide is obtained by the precipitation of a soluble zinc salt by an alkali hydroxide. In an excess of the reagent the precipitate dissolves, forming a zincate, as K_2ZnO_2.

Zinc Chloride, $ZnCl_2$, is an important salt formed by the solution of the metal in hydrochloric acid, also in anhydrous condition by distilling a mixture of $ZnSO_4$ with $CaCl_2$. The solution is used largely in the impregnation of wood for preservation and also as a deodorizer and disinfectant. The anhydrous salt is employed in organic experimental chemistry because of its marked power of absorbing water and thus bringing about certain combinations. Zinc chloride can be volatilized under conditions which permit a determination of its vapor density.

Zinc Sulphate. In crystallized form this salt is known as white vitriol, $ZnSO_4.7H_2O$. It is easily made by dissolving zinc in dilute sulphuric acid, and is very soluble

in water. Many other zinc preparations are made from this salt. It is isomorphous with Epsom salt, $MgSO_4 . 7H_2O$.

Among other zinc compounds the sulphide, ZnS, and the carbonate, $ZnCO_3$, may be mentioned. The first is a white precipitate obtained by action of ammonium sulphide on a soluble zinc salt. It is readily soluble in weak mineral acids. The second is obtained in impure condition by precipitating soluble zinc salts by alkali carbonates.

Recognition. The precipitation of the sulphide and carbonate, just referred to, may be employed in the testing for zinc. The formation of a white hydroxide, which dissolves in excess of the precipitant, is also valuable as a test.

CADMIUM.

Occurrence. This metal is usually found as sulphide with zinc sulphide, and also in other zinc ores, but not in large amount. A pure sulphide, CdS, occurs as a rare mineral.

History and Preparation. The metal was discovered in 1818 as a constituent of crude zinc. As it is much more volatile than zinc it separates and distills first in the usual process of obtaining that metal, explained above. By repeated distillation the metal may be obtained practically free from zinc.

Properties and Uses. It is tough and somewhat malleable, standing between zinc and lead in hardness. It forms readily a number of alloys, some of which have a very low melting point.

The salts of cadmium are not important. The sulphide, CdS, is a yellow pigment; the iodide, CdI_2, is a heavy salt sometimes used in making photographic emulsions. The chloride, $CdCl_2$, and the sulphate, $CdSO_4$, are easily made by solution of the metal in hydrochloric or sulphuric acid.

Recognition. The salts of cadmium yield a yellow precipitate with hydrogen sulphide or ammonium sul-

phide which is not soluble in an excess of alkali sulphide. Cadmium hydroxide, CdO_2H_2, is a white precipitate obtained by adding an alkali hydroxide to a cadmium solution. It is soluble in an excess of ammonia water.

MERCURY.

Occurrence. The native metal is found in small quantity, but the important ore is the red sulphide or cinnabar, HgS. This is mined in California, in Spain, in the Austrian province of Carniola and elsewhere. The world's production in 1903 was 3,601 metric tons, of which the United States furnished 1,288 tons, Spain 968 tons and Austria 523 tons.

History. Mercury was known to the Greeks and early Latin writers; but its importance was not great until the time of the alchemists, who studied its properties. Because of its numerous uses in physical and chemical researches, its properties have been carefully investigated in modern times by many scientists.

Metallurgy. The metal is usually separated by distillation of the sulphide with lime in iron retorts, or by the action of hot gases from the combustion of fuel on the ore in furnaces of peculiar construction.

In this case the sulphur burns to SO_2 and the mercury is liberated, to be condensed in long, tight chambers connected with the furnace.

Properties. This is the only metal liquid at the ordinary temperature. It boils at 357° C. and at —39° becomes solid. The rate of expansion by heat is very regular for mean ranges of temperature, being 0.0001815 of the volume at 0° for each degree. For higher temperatures the rate of expansion increases but slightly, upon which fact the value of the metal in constructing accurate thermometers partly depends. As it may be easily distilled the purification is not difficult, and the metal may therefore be brought into a condition of constant composition, essential in any substance employed as a standard. The important unit of electrical resistance

is based on the resistance of a column of pure mercury of certain dimensions.

The metal unites readily with many other metals, forming mixtures called amalgams.

Uses. Mercury is used largely in the extraction of gold and silver by amalgamation, already referred to. It is employed in the construction of thermometers, barometers, pressure gauges and many other instruments for scientific and technical measurements. The amalgams are very useful; one with tin serves for the backing of mirrors, some with cadmium and tin and also other metals are used in filling teeth, while other combinations find different applications in the arts.

Compounds of Mercury. Like copper, mercury forms two series of compounds, the mercurous and mercuric, some of which find extensive use in medicine.

Mercury Oxides. Mercurous oxide, Hg_2O, is a black powder formed by precipitation of a mercurous salt by solution of KOH, or by digesting calomel, HgCl, with this alkali. It oxidizes readily, and on standing decomposes partly into mercury and mercuric oxide. This oxide, HgO, is obtained by heating mercury in the air to about 300° to 350°, also by calcining the nitrate. A crystalline red powder is made in these processes, and this has been used in experiments, already given, on the liberation of oxygen. By precipitating mercuric chloride with potassium hydroxide an amorphous yellow oxide is obtained.

Mercuric Sulphide, HgS, is obtained as a black precipitate by passing H_2S into a solution of a mercuric salt. When this precipitate is dried and sublimed it turns red. A red sulphide, called *vermilion,* is made directly by subliming a mixture of mercury or mercuric oxide with sulphur. It is used as a valuable red pigment, and is identical in composition with the native cinnabar. Mercurous sulphide cannot be obtained by precipitation of mercurous compounds by hydrogen sulphide.

Mercury Chlorides. Mercurous chloride, $HgCl$, is commonly known as calomel and is made by subliming an intimate mixture of mercury and corrosive sublimate which have been well rubbed together. It is an amorphous white powder, insoluble in water, and is largely used in medicine, the sublimed mass being prepared for this purpose by grinding and thorough washing with water to remove any of the other chloride carried over. Mercurous chloride turns black by the addition of ammonia water. Mercuric chloride, $HgCl_2$, is known as corrosive sublimate and is usually made by distilling a mixture of common salt and mercuric sulphate. It is a white, crystalline mass, soluble in water, and violently poisonous. With ammonia it yields a white precipitate:

$$HgCl_2 + 2NH_3 = NH_4Cl + HgClNH_2$$

This chloride is largely used in the sterilization of surgical instruments before and after use, and in the disinfection of articles which have been exposed to contagion. A solution of 1 part to 1,000 or 2,000 of water is sufficient for such purposes. Steel instruments are, however, corroded by the solution. It is readily soluble in glycerol, and this solution is often used in the preparation of aqueous solutions by dilution.

Mercury Iodides. Mercurous iodide, HgI, may be obtained as a green mass by rubbing mercury and iodine together in a mortar in proper proportions. It is also made by precipitation of mercurous nitrate by a solution of potassium iodide. It is not very stable. Mercuric iodide, HgI_2, is a beautiful bright red precipitate obtained by adding potassium iodide solution in right amount to a mercuric solution:

$$2KI + HgCl_2 = 2KCl + HgI_2$$

The precipitate is readily soluble in an excess of the potassium iodide, and the solution so obtained is a valuable laboratory reagent. The iodide may be sublimed at a high temperature.

Other Compounds. Mercuric sulphate, $HgSO_4$, is made by solution of mercury in strong sulphuric acid. It serves for the preparation of the chloride. By treating with boiling water it is converted into a yellow basic salt known as turpeth mineral, $HgSO_4.2HgO$. Mercuric nitrate, $Hg(NO_3)_2$, is made by action of strong nitric acid on mercury; with a weak acid in the cold mercurous nitrate, $Hg(NO_3)$, is obtained.

Recognition. Mercury in compounds may be recognized by the separation of the metal as a bright amalgam when a copper wire or bit of foil is rubbed with some of the substance mixed with hydrochloric acid. In solid bodies it may be easily detected by fusion with a mixture of dry sodium carbonate and saltpeter in a glass tube. The volatile metal is liberated and condenses in droplets on the cooler upper part of the tube.

CHAPTER XVIII.

BORON. ALUMINUM. GALLIUM. INDIUM. THALLIUM. SCANDIUM. YTTRIUM. LANTHANUM AND YTTERBIUM.

GENERAL CHARACTERISTICS.

These elements form the third family in the Periodic System and with three exceptions are technically quite unimportant. The compounds of boron have been referred to already, while those of aluminum will be briefly described below. A few thallium compounds are somewhat important, while those of the other elements are very rare. The chief physical properties are shown in the following table:

	Atomic Weight.	Specific Gravity.	Atomic Volume.	Melting Point
Boron	11.0	2.68	4.1	high
Aluminum	27.1	2.60	10.3	700°
Gallium	70.0	5.95	11.7	30°
Indium	115.0	7.42	15.3	176°
Thallium	204.1	11.86	17.2	290°
Scandium	44.1			
Yttrium	89.0			
Lanthanum	138.9	6.20	22.3	
Ytterbium	173.0			

The nine elements in this family fall naturally into two groups: a primary group containing scandium, yttrium, lanthanum and ytterbium, and a secondary group containing boron, aluminum, gallium, indium and thallium. With the exception of boron they behave in their best known compounds as metals and are all trivalent. Thallium is closely related to the alkali metals on the one

hand and to lead on the other, but it is usually placed in this group. It will be recalled that the metallic character of the elements in the horizontal periods diminishes on passing from left to right in the table of the periodic arrangement; we have in boron the first of the elements in which the acid behavior is quite marked. In the next family the change will be found still more characteristic.

ALUMINUM.

Occurrence. This metal is very abundant in combination. It is found as silicate in all clay and in more or less pure condition in several other minerals, as the felspars, $AlKSi_3O_8$ and $AlNaSi_3O_8$. It occurs as oxide, Al_2O_3, in corundum, ruby, sapphire and emery; as hydroxide or basic hydroxide in several minerals of which bauxite, $Al_2O(OH)_4$, is the most important; as fluoride in cryolite, $AlF_3.3NaF$. Clays, which are crude, hydrated silicates, are formed by the weathering or disintegration of felspars and similar silicates.

History. The important properties of the alums were known to the alchemists, and over one hundred years ago it was recognized that a peculiar earth is combined with sulphuric acid in these bodies. In his important electrical work Davy, early in the nineteenth century, tried to separate the metal which he believed this earth must contain, but without success. In 1827 Woehler succeeded in isolating the metal by decomposing the chloride by means of potassium:

$$AlCl_3 + 3K = 3KCl + Al$$

Metallurgy. For many years all the aluminum of commerce was made by a process based on the above reaction. Potassium was replaced by sodium and great improvements were made in the methods of producing the chloride, $AlCl_3$, but at best the processes were expensive and the metal found but limited applications. Recently, methods have been perfected by which the reduction is effected through the agency of the electric

current. The electric furnace in which this reduction is carried out is a large iron box lined with carbon. In this is placed a mixture of powdered cryolite and carbon and a powerful current is passed in through massive anodes of hard carbon, the box itself serving as the cathode. The cryolite is fused by the intense heat generated by the passage of the current, and then powdered alumina, made from bauxite, is added from time to time. This is decomposed into metal and oxygen, the former sinking to the bottom of the box or furnace, from which it is drawn off from time to time, while the latter is taken up by the carbon of the bath and of the anodes. The reaction may be explained as one of electrolysis, or, on the other hand, it may be considered as one between carbon and alumina, Al_2O_3, made possible by the high heat between the electrodes. In some of the later modifications of the electric furnace method aluminum of a high degree of purity is produced.

In 1903 the United States produced 3,000,000 kilograms of aluminum, France about 1,400,000 kilograms, Switzerland about 2,500,000 kilograms and Germany about 1,200,000 kilograms.

Properties. Aluminum is a white, malleable and ductile metal, comparatively soft and not easily corroded in the air or by acid fumes. Even at a high temperature it oxidizes but imperfectly. At a red heat it decomposes steam. Nitric and sulphuric acids attack it but slowly, but in hydrochloric acid it dissolves readily. With potassium or sodium hydroxide it forms an aluminate, with liberation of hydrogen. Aluminum alloys with a number of metals; with copper it forms a valuable bronze called aluminum bronze.

Uses. Because of its low specific gravity and resistance to oxidation the metal has come into use for the manufacture of numerous small articles, such as beams of balances, handles of surgical instruments, combs and backs of brushes, buckles and even cooking utensils. It was at one time predicted that the metal would come into use for structural purposes, in place of iron, but these

expectations have not been realized. It is a relatively good conductor of electricity and on account of its low specific gravity and low cost it is used in the form of very thick wire to carry heavy currents long distances.

A mixture of aluminum powder and certain metallic oxides may be readily ignited and burns with great intensity. Aluminum acts as a reducing agent, and the oxide used is brought to the metallic condition. The intense heat obtained is often employed in welding operations. The powder mixture is known as thermit.

Aluminum Oxide. This is found in nature in several forms, as mentioned above. The ruby and the sapphire have also been formed artificially. The cheaper emery is commonly used for grinding and polishing metals and glass, as it is extremely hard. Amorphous aluminum oxide may be easily made by precipitating the hydroxide, $Al(OH)_3$, washing it thoroughly and finally heating to a high temperature. It is left in this way as a white substance quite insoluble in water, and but slowly soluble in acids.

Aluminum Hydroxides. The simple, normal hydroxide, $Al(OH)_3$, is made as a laboratory product:

$$Al_2(SO_4)_3 + 6NH_4OH = 2Al(OH)_3 + 3(NH_4)_2SO_4$$

As so made it is a white, gelatinous mass. In nature several hydroxides occur, the most important being bauxite. In this, part of the aluminum is usually replaced by iron giving bodies varying between $Al_2O(OH)_4$ and $AlFeO(OH)_4$. The varieties low in iron are used in the manufacture of the alums and the metal itself. The world's production of bauxite in 1902 was about 140,000 metric tons.

Aluminum Chloride. This is easily obtained in solution by dissolving the metal or hydroxide in hydrochloric acid. The pure, dry substance is made by passing dry chlorine gas over a heated mixture of aluminum oxide and charcoal, or, better, by passing dry chlorine over hot

aluminum turnings, in a tube heated in a gas furnace. When obtained in this way it is a solid, colorless substance which may be vaporized at a moderately high temperature. The density of the vapor taken at a sufficiently high temperature gives $AlCl_3$ as the formula, suggesting the trivalent character of the metal. The chloride is a valuable agent in organic synthesis.

Aluminum Sulphate. As the group SO_4 is bivalent and aluminum trivalent, the formula of this salt is $Al_2(SO_4)_3$. It is usually made by dissolving the hydroxide from bauxite in dilute sulphuric acid. The evaporated liquid yields the salt with a large amount of combined water. This product, or one more completely evaporated, is used for several purposes in the arts, especially in the clarification of water, as a mordant in dyeing and in the glazing of paper. It is also used in the manufacture of some of the common alums.

The Alums. Aluminum sulphate combines with alkali sulphates and water, forming bodies of the following composition:

$$KAl(SO_4)_2 + 12H_2O$$
$$NaAl(SO_4)_2 + 12H_2O$$
$$NH_4Al(SO_4)_2 + 12H_2O$$

These are called alums, the first and third being common commercial substances. As they crystallize well, they may be easily purified, which is not the case with the very soluble aluminum sulphate. These alums are often used in the place of the simple sulphate, and may be made from several other substances than bauxite as a starting material.

The term alum is applied to a large number of double sulphates besides those containing aluminum. Thus, chrome alum is $KCr(SO_4)_2 + 12H_2O$; ferric alum is $NH_4Fe(SO_4)_2 + 12H_2O$. In general, an alum is a double sulphate formed by combining an alkali metal (Li, Na, K, Cs, Rb, NH_4), and a trivalent metal (usually Al, Fe or Cr) with two SO_4 groups and 12 H_2O. These alums are isomorphous and crystallize in octahedra. It

is a further interesting fact that the analogous selenates and tellurates belong to the same isomorphous group.

Aluminum Silicates. These occur in nature in a great number of minerals. Kaolin is nearly pure aluminum silicate, while clay is a mixture in which this silicate largely predominates. These bodies are used in the production of articles of earthenware or pottery in various forms. The finer pottery known as porcelain is made of the purest kaolin, while other kinds are made of commoner material.

Pottery.

In the manufacture of pottery the clay or kaolin to be used is ground to a fine powder which is mixed with some powdered material to serve as a flux. This is often felspar, or it may be a mixture of chalk or gypsum with quartz. Pure clay does not fuse, even at a very high temperature, and the flux is employed to melt, surround the clay particles and bind them together. To this end the prepared mixed material is ground up with water to form a smooth, homogeneous mass, which is molded into the desired articles. These are dried and gradually heated to a high temperature, by which a more or less porous product known as biscuit ware is obtained. For many purposes this ware cannot be employed, but must be covered with a glaze. In some cases, to secure this, the articles are covered with a paste containing litharge and reheated, by which a smooth lead silicate is formed and flows over the whole mass. A so-called salt glaze is produced on some kinds of cheaper wares by throwing salt into the kilns in which the biscuit or open ware is fired, just before the end of the operation. This volatilizes and is decomposed, yielding finally a fusible sodium-aluminum silicate to flow over the whole surface. Mixtures of quartz, chalk and borax are used in some glazes. For hard laboratory porcelain a mixture of kaolin, quartz, lime and broken porcelain is often used. When this is fused over the fine biscuit ware a smooth, hard surface is secured which is intended to resist the action of chemicals.

Other Compounds. Cryolite is a double fluoride having the composition $AlF_3.3NaF$. It is used in the metallurgy of aluminum, also to produce sodium carbonate and for its fluxing properties in general. Ultramarin is a complex mixture obtained by fusing kaolin with sodium sulphate and carbon, or with sulphur and sodium carbonate. The composition is variable, but one kind has approximately the formula $Al_2Si_2Na_3SO_8$. Aluminum acetate is used as a valuable mordant in dyeing. Aluminates may be formed by solution of the metal or hydroxide in caustic alkalies, or by fusion of the hydroxide with caustic or carbonate alkali.

Experiment 168. Place some bits of aluminum wire in a test-tube and add solution of sodium hydroxide. A slow evolution of hydrogen gas begins, which is hastened by application of heat. The metal dissolves to form sodium aluminate, $NaAlO_2$.

Recognition. The aluminum in soluble compounds is easily recognized by the white precipitate of hydroxide formed on the addition of ammonia water. This precipitate is soluble in an excess of caustic soda or potassa solution.

GALLIUM AND INDIUM.

These are two very rare metals found in the zinc blendes of certain localities. Both were discovered by aid of the spectroscope, the former in 1875 by L. de Boisbaudran, and the latter by Reich and Richter in 1863. Gallium melts at 30° C., that is below the body temperature, and is characterized by the two blue violet lines it shows in the spectrum. Indium shows likewise two blue lines in the spectrum. Both metals behave as trivalent in most of their compounds, and both form alums, and several other compounds resembling those of aluminum.

THALLIUM.

Occurrence and History This comparatively rare metal is found in certain iron and copper pyrites and in a few other minerals. It was discovered in 1861 by Crookes in the examination of a deposit from the lead chambers of a German sulphuric acid factory where

pyrites were burned to furnish the sulphurous oxide. It is prepared usually from similar deposits.

Properties. Thallium is a soft metal resembling lead in appearance and in physical properties. But it oxidizes in moist air yielding an oxide, Tl_2O, which dissolves in water with formation of an alkaline hydroxide, TlOH. In this behavior it resembles the alkali metals. It decomposes water at an elevated temperature and dissolves readily in dilute sulphuric acid.

Uses. The metal has no technical applications, but several of its compounds are practically useful. Some of them are used in making a very dense glass with high refractive index, for optical purposes.

Compounds of Thallium. Some of these resemble the corresponding lead compounds closely, while others are similar to the compounds of the alkali metals. In a few salts a resemblance to the aluminum salts is found. From these conditions it is evident that the proper place of this metal among the elements is hard to define. Two classes of compounds are known, some being univalent, the others trivalent. TlCl, TlBr and TlI are insoluble bodies resembling the lead and silver salts. TlOH and Tl_2SO_4 are soluble and in some respects similar to KOH and K_2SO_4. The sulphate forms an alum with $Al_2(SO_4)_3$. On the other hand, we have thallic sulphate, $Tl_2(SO_4)_3$, which combines with potassium sulphate to form an alum-like body. Thallous hydroxide, TlOH, is colored brown by ozone, and paper moistened in such a solution is sometimes used as an ozone test.

Recognition. Thallium compounds are easily recognized by the bright green line they exhibit in spectroscopic examination.

THE RARE EARTHS.

Several complex minerals are known which contain a number of closely related metals, the oxides of which are spoken of as the rare earths. One of these minerals

is called gadolinite; it is a silicate of yttrium and a dozen other metals in smaller proportion. Another mineral is known as euxenite, which contains scandium, ytterbium and several other metals in combination with titanic acid. Lanthanum is found in these minerals and in several others. The separation of all the metals contained in these complex compounds is a matter of extreme difficulty, and the problem cannot as yet be considered as completely solved. Something more will be said about these bodies in the following chapter, where some important technical applications of several related earths will be explained.

CHAPTER XIX.

THE CARBON GROUP: CARBON, SILICON, GERMANIUM, TIN AND LEAD.—THE TITANIUM GROUP: TITANIUM, ZIRCONIUM, CERIUM AND THORIUM.

GENERAL CHARACTERISTICS.

The fourth family of the Periodic System contains a number of elements of which the nine above given have been pretty thoroughly studied. Carbon and silicon have been already described, as fully as is necessary for our purpose, in the ninth and eleventh chapters. In the present chapter they are introduced again merely to show their relations to the other members of the family. It is customary to divide this family into two groups, but the division is somewhat arbitrary. In the following table the important physical constants of the elements are given:

	Atomic Weight.	Specific Gravity.	Atomic Volume.	Melting Point.
Carbon	12.0	3.50	3.4	very high
Silicon	28.4	2.49	11.4	very high
Germanium	72.5	5.47	13.2	900°(?)
Tin	119.0	7.29	16.3	233°
Lead	206.9	11.40	18.1	326°
Titanium	48.1	3.70	13.0	very high
Zirconium	90.6	4.15	21.7	1500°(?)
Cerium	140.25	6.70	20.8	800°(?)
Thorium	232.5	11.20	20.8	very high

The family likeness of these elements may be illustrated by collecting the formulas of some of their best known compounds.

CO_2	CS_2	CH_4	CCl_4	
SiO_2	SiS_2	SiH_4	$SiCl_4$	$Si(OH)_4$
GeO_2	GeS_2		$GeCl_4$	
SnO_2	SnS_2		$SnCl_4$	
PbO_2			$PbCl_4$	
TiO_2	TiS_2		$TiCl_4$	$Ti(OH)_4$
ZrO_2			$ZrCl_4$	$Zr(OH)_4$
CeO_2				
ThO_2	ThS_2		$ThCl_4$	$Th(OH)_4$

It will be noticed that in the groups of oxides, sulphides and chlorides there is an almost complete parallelism. Bromides and fluorides of the type MX_4 are known for most of the elements in the list.

The acid character of some of these elements is very pronounced, as seen in the carbonates and silicates. Stannates and titanates of the light metals are known; with germanium, lead and thorium the metallic character predominates.

GERMANIUM.

This is a very rare element which was discovered in 1886 in a silver ore. It is sometimes observed in tin ores but only in small amount. Like tin, it forms two series of salts; in the first it is bivalent and in the other quadrivalent.

TIN.

Occurrence. This important metal has been found in several ores, but the valuable ore is tinstone or cassiterite, SnO_2, which occurs in Cornwall, in Australia, in the Island of Banca, in the Malay Peninsula, in Bolivia and elsewhere. A tin pyrite is also known but it is not abundant.

History. Tin was known in very early times, and it appears that before the beginning of the Christian era the mines or deposits of Cornwall were worked by the peoples living around the eastern shores of the Mediterranean. It was largely used in making bronze and in

soldering lead. The properties and uses of tin were well known to the alchemists, and possibly even before their time its value as a coating for iron was known. This knowledge was not applied practically until about 1720, however. To-day this is the most important use to which tin is put.

Metallurgy. Tinstone is a very hard ore and somewhat difficult to reduce. Several reactions have been employed in separating the metal, but now it is commonly reduced by carbon in a blast furnace or in a kind of reverberatory furnace. The ore is stamped and washed to separate earthy matter and roasted to convert sulphides into oxides. So prepared it is ready for the actual reduction:

$$SnO_2 + 2C = Sn + 2CO$$

The crude tin which is run from the hearth of the reverberatory furnace or from the blast furnace may contain iron, copper and traces of other metals. This is refined by the process termed liquation, in which the crude blocks or ingots are piled up in a reverberatory furnace with inclined hearth, the metal being at the highest part of the incline. As tin is readily fusible it begins to flow out from the mass when the furnace is gently and gradually heated. The other metals require greater heat for melting and remain behind in the operation.

The purest tin comes from Banca. The world's production of tin in 1902 was 93,002 metric tons, of which about 20,000 tons came from the Malay Peninsula, and 17,000 tons from Bolivia.

Properties. Tin is a white metal which melts at about 233°. It is malleable and ductile at a temperature of 100°. At a temperature of 200° it becomes so brittle that it may be easily powdered. At low temperatures also it is very brittle. It alloys easily with several other metals, and resists atmospheric effects in a marked manner. A bar of tin when bent emits a peculiar sound called the "cry of tin."

Uses. It is employed mainly in coating iron and copper. The metal to be covered is thoroughly cleaned and dried and dipped in a bath of molten tin. Enough clings to form a good, durable coating. Several common alloys contain tin. Pewter is a mixture of about 4 parts of tin with 1 of lead; common solder contains lead and tin in equal proportions; bronze, bell metal, speculum metal and gun metal are essentially tin and copper alloys. Tin amalgam is used in silvering mirrors.

Tin Oxides. Two are known. The monoxide, SnO, is unimportant; the dioxide, SnO_2, is the common ore of tin. An artificial product which is perfectly white is made by oxidizing tin with nitric acid and heating the residue. It is quite insoluble in water. When this oxide is fused with sodium hydroxide a soluble salt known as sodium stannate is produced. It has the composition Na_2SnO_3, and is used as a mordant in calico printing. Hydroxides of tin are also known.

Tin Sulphides. Stannous sulphide, SnS, may be made by heating a mixture of tin foil and sulphur; also by precipitation of a solution of stannous chloride by hydrogen sulphide. This yields a brown precipitate which becomes darker on drying. The disulphide, SnS_2, is an important substance made usually by subliming a mixture of tin amalgam, sulphur and ammonium chloride. The mercury and chloride are driven off in the sublimation while the tin remains in yellow scales as disulphide. When prepared in this way the product is known as mosaic gold and is used as a bronze powder for many purposes. A yellow precipitate of amorphous SnS_2 is obtained by passing hydrogen sulphide into an acid stannic solution.

Tin Chlorides. Stannous chloride, $SnCl_2$, is obtained by dissolving tin in hydrochloric acid. On evaporating the solution a crystalline compound, $SnCl_2.2H_2O$, separates. Under the name of *tin salt* this is used as a mordant in dyeing. A solution of stannous chloride is a valuable reagent in the laboratory. Stannic chloride, $SnCl_4$, is a fuming, colorless liquid obtained by passing chlorine

over melted tin. It is readily soluble in water, yielding hydrates, $SnCl_4.3H_2O$ and $SnCl_4.5H_2O$, with proper amounts of water. These hydrates are obtained in solid crystalline condition, the first being known as *butter of tin*. They are employed as mordants to produce certain colors in dyeing. When used for this purpose they are most easily made by dissolving tin in aqua regia, evaporating and crystallizing from water.

Other Compounds. Bromides and iodides of tin corresponding to the two chlorides are known. Nitrates and sulphates have been made, but they are without importance and are not stable.

Recognition. Tin compounds are recognized by the hydrogen sulphide precipitates, and by the separation of the metal when zinc is added to a tin solution containing a little hydrochloric acid. Stannous chloride reacts with mercuric chloride in this way, to give first a white precipitate of calomel and finally a dark gray precipitate of metallic mercury:

$$SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl$$
$$SnCl_2 + 2HgCl = SnCl_4 + 2Hg$$

LEAD.

Occurrence. This metal occurs usually as the gray sulphide, or galena, PbS. It is found also as native lead in small amount, and in rare minerals as oxide, carbonate, sulphate, chromate and chloride. Galena is found very widely distributed and is especially abundant in the United States.

History. This is one of the seven metals known to the peoples of antiquity, and crude methods were employed to reduce it from the sulphide. In their northern conquests the Romans introduced the knowledge of smelting in the countries where the ore was found. The development of the modern methods of smelting has been gradual.

Metallurgy. Galena is reduced by several distinct methods. In one the ore is heated in a furnace with iron, which takes the sulphur and leaves the lead in the free state. In a modification of this process the ore is heated with a mixture of iron oxide and coke in a blast furnace. The iron oxide becomes reduced to spongy iron, which acts readily on the galena. In a second method of smelting the lead sulphide is roasted in a reverberatory furnace to form a mixture of oxide and sulphate, leaving a part of the galena unchanged. In a second stage of the process the heat of the furnace is increased and the excess of air shut off; then the three substances react on each other in this way:

$$2PbO + PbS = 3Pb + SO_2$$
$$PbSO_4 + PbS = 2Pb + 2SO_2$$

The metallic lead collects on the hearth of the furnace, from which it is run off from time to time.

At the present time in this country a large part of the lead is obtained in the smelting of ores which contain gold and silver also. This is done in a blast furnace with coke, using such a mixture of ores as will best furnish a liquid slag and permit a separation of the lead and precious metals present, as was explained in the fifteenth chapter. It was further explained how the crude lead bullion obtained is desilverized and softened and made ready for commerce.

In 1902 the world's production of lead was about 027,000 metric tons, of which the United States furnished 254,489 metric tons, Spain 177,560 metric tons and Germany 140,331 metric tons.

Properties. Lead is a soft metal, malleable, but not very ductile. It is not corroded to a great extent in the air, and in water only under certain conditions. Ordinary hard waters have but little action, while soft waters containing carbonic acid or much chloride or nitrate dissolve it appreciably. Such waters should not be conveyed through lead pipes for household use. The metal alloys

readily with several others. It is but slightly attacked by sulphuric acid and only slowly by the other mineral acids.

Solutions of lead are reduced by several metals, notably by zinc, which can be illustrated as follows:

Experiment 169. Fill a bottle with a very dilute solution of lead acetate in distilled water, and immerse in it a thin strip of sheet zinc, cut and spread to represent the branches of a tree. Bend the upper end of the zinc so that it may hang over a glass rod resting on the neck of the bottle. At the end of twenty-four hours a crystalline deposit of the lead in the form of thin, glistening plates appears, suspended from the branches of the zinc. This is called the *lead tree* and is formed best when the solution is dilute and the deposition, in consequence, slow.

Uses. Lead is employed in sheet form for many purposes, especially in lining the chambers in which sulphuric acid is made. As pipe it is used to convey water. Ordinary shot consists of lead frequently alloyed with a fraction of a per cent of arsenic. Type metal is an alloy of antimony and lead, with tin sometimes added. Common solder is an alloy of lead and tin. Several important easily fusible alloys contain lead, bismuth and tin.

Considerable quantities of lead are also used in making the plates of storage batteries. Although these are very heavy and have other disadvantages nothing better has been found to replace them.

Lead Oxides. Three are well known.

Litharge, PbO, is a yellow substance obtained by oxidizing lead in the air. If the temperature is kept below 800° the product is in the form of a powder, but at a somewhat higher temperature this melts and forms a hard solid on cooling. This oxide is used in making several lead salts and largely in the manufacture of glass of certain kinds. *Red lead*, Pb_2O_3 or Pb_3O_4, is formed by heating litharge in the air. Oxygen is absorbed to form what may be considered as a mixture of PbO and PbO_2. It is used as a pigment to some extent, also in varnishes and in the glass industry instead of litharge. It is also used in cements. *Lead peroxide*, PbO_2, is made by action of nitric acid on red lead, by which means the PbO is dis-

solved out. It may also be made by action of bleaching powder on lead chloride and is valuable as an oxidizing agent in technology and in the laboratory. Several hydroxides are known, but they are not specially important.

Lead Sulphide occurs as galena and may be obtained by precipitation of a lead salt with hydrogen sulphide. This is a black precipitate, but if the solution contains much free hydrochloric acid a reddish chlorosulphide is obtained.

Lead Carbonates. Several are known, but the basic carbonate, a mixture of $PbCO_3$ and $Pb(OH)_2$, is the important one and is known as *white lead*. This is made by a number of processes, but the so-called Dutch process yields the best product. In this, sheets of corrugated lead are placed in stoneware jars with a little vinegar and these jars are imbedded in rows in spent tanbark, but covered so as to exclude contamination. The spent bark evolves CO_2 and this, acting on the basic acetate of lead formed in the jars, converts it into basic carbonate. The heat generated by the fermentation of the bark is an important factor in the formation of the basic acetate. The whole operation is a slow one, requiring several weeks for completion. At the end of this time the jars are carefully uncovered and emptied into sifting machines, where the pure white lead is separated from any of the metal not corroded. The product is ground with water to a uniform cream, dried and sold in this form, or ground in oil. It is the most valuable white pigment we have, but is often adulterated with cheaper products.

Lead Chloride, Bromide and Iodide are compounds which are soluble in boiling water, but only slightly soluble in cold water. Their hot, concentrated solutions, therefore, deposit crystalline precipitates on cooling. The formulas are $PbCl_2$, $PbBr_2$ and PbI_2.

Lead Sulphate, $PbSO_4$, is a white substance, insoluble in water, and only slightly soluble in acids. It is frequently used as a pigment, but this has less value than the carbonate.

Lead Nitrate is made by dissolving litharge in nitric acid. It is a soluble salt and is used in making other lead compounds by precipitation, and also as a mordant by the dyer.

Lead Chromate, $PbCrO_4$, is known as chrome yellow. It is made by precipitating the nitrate or acetate by a solution of potassium dichromate and is used as a pigment. Chrome orange is basic lead chromate.

Lead Acetate, $Pb(C_2H_3O_2)_2$, is the most valuable soluble compound of lead. It crystallizes with $3H_2O$ and so comes into commerce. A solution of this salt in water has the power of dissolving large amounts of litharge, forming solutions of basic lead acetate, or subacetate. All of them have important applications.

Toxicity. The soluble salts of lead are violent poisons when taken internally in sufficient quantity. Workmen in white lead mills suffer also from a peculiar kind of lead poisoning, and with painters who use lead paints something similar is observed. Because of this toxicity zinc oxide is taking the place of white lead in many pigments.

Recognition. Lead compounds are recognized by the white precipitate of sulphate formed by the action of soluble sulphates, by the black sulphide formed in their solutions on addition of hydrogen sulphide or ammonium sulphide, or by the precipitation of white lead chloride on addition of a soluble chloride. This last precipitate dissolves by heating, but comes down in crystalline needles on cooling.

TITANIUM.

Although not abundant, this metal is widely distributed, occurring as dioxide, TiO_2, in rutile and two other minerals, and also with oxides of iron and other ores. It is therefore a constituent, in small amount, of some cast irons. The metal may be obtained in the free state, but is not technically useful. In some of its compounds it acts the part of a true metal, forming well defined halo-

gen and other salts, while in other compounds it acts as titanic acid, yielding titanates resembling the stannates. The metal combines directly with nitrogen at a high temperature.

ZIRCONIUM.

This is a comparatively rare metal, found in the mineral zircon, $ZrSiO_4$, and in other even rarer minerals. The dioxide, ZrO_2, becomes incandescent when heated, and has been used in making lamps; but these have been displaced largely by the lamps in which oxide of thorium is employed.

CERIUM.

This metal occurs in a few rare minerals, of which *monazite*, a complex phosphate of cerium, thorium and lanthanum, *cerite*, a silicate of cerium, lanthanum and other metals, and *orthite*, a silicate of aluminum, cerium, iron and calcium, are the most important. The oxides of cerium and several associated metals are commonly spoken of as the *cerite earths*. Interest attaches to these bodies mainly because of their use in the construction of lamps for illumination by gas by incandescence. One of the salts of cerium, the oxalate, is used in medicine.

THORIUM.

This rare metal is found in *monazite*, mentioned above, and also in *thorite* and *orangeite*, which are complex silicates. The metal itself has no technical value, but its dioxide, ThO_2, has become of immense importance because of its power of emitting a brilliant white light at a relatively low temperature. The body which becomes incandescent is a gauze-like skeleton, cone or mantle of thorium dioxide mixed with a small amount of cerium oxide with traces, often, of the oxides of yttrium, neodymium and zirconium. To obtain this skeleton, cotton gauze woven or cut to the desired size and shape is immersed in a solution of the prepared thorium nitrate. It is then dried and carefully ignited, by which means water, oxides of nitrogen, and organic matter are expelled, leaving the metallic oxides in the shape of the original cotton gauze

skeleton. When this is properly supported in the colorless gas flame, that of a Bunsen burner, for instance, it becomes brightly incandescent. It has been shown that thorium oxide alone does not yield the brightest light, but that this is secured by the presence of the cerium oxide.

The great demand for thorium nitrate has led to the search for new minerals and sources are now known which were not suspected some years ago. The production of monazite in the United States in 1903 was about 400,000 kilograms.

CHAPTER XX.

THE NITROGEN GROUP OF ELEMENTS: NITROGEN, PHOSPHORUS, VANADIUM, ARSENIC, COLUMBIUM, ANTIMONY, TANTALUM AND BISMUTH.

GENERAL CHARACTERISTICS.

The important properties of some of the elements of this, the fifth family or group in the Periodic System, have been discussed already. It remains to point out family resemblances here and to describe briefly the compounds of the remaining important elements. In their chemical behavior the first elements in the family are decidedly acid, while as before observed in other groups, with increase in atomic weight the elements become decidedly metallic. The physical constants, so far as known, are shown in the table below:

	Atomic Weight.	Specific Gravity.	Atomic Volume.	Melting Point.
Nitrogen	14.04			—200°
Phosphorus	31.0	1.83	16.9	44.2°
Vanadium	51.2	5.50	9.3	very high
Arsenic	75.0	5.73	13.1	500°
Columbium	94.0	7.20	13.0	very high
Antimony	120.2	6.71	17.9	630°
Tantalum	183.0	10.60	17.2	very high
Bismuth	205.5	9.82	21.2	268°

The elements of the group are in most of their compounds trivalent or pentavalent, as the following table illustrates. The parallelism between nitrogen and vanadium is further shown by the series of oxides formed, these five being known: V_2O, V_2O_2, V_2O_3, V_2O_4 and V_2O_5.

NH_3	NCl_3	N_2O_3		N_2O_5	HNO_3
PH_3	PCl_3	P_2O_3	PCl_5	P_2O_5	HPO_3
	VCl_3	V_2O_3		V_2O_5	HVO_3
AsH_3	$AsCl_3$	As_2O_3		As_2O_5	$HAsO_3$
	$CbCl_3$		$CbCl_5$	Cb_2O_5	$HCbO_3$
SbH_3	$SbCl_3$	Sb_2O_3	$SbCl_5$	Sb_2O_5	$HSbO_3$
			$TaCl_5$	Ta_2O_5	$HTaO_3$
	$BiCl_3$	Bi_2O_3		Bi_2O_5	$HBiO_3$

In the last column of the table above the formulas of the meta acids corresponding to the pentoxides are given. With the first in the series, HNO_3, the acid properties are very strong, while with the last, $HBiO_3$, they are quite absent. The others show acid behavior decreasing in character as we pass down in the series. Salts of all these acids are known until we reach the last.

VANADIUM.

This rare element is found in the form of lead and bismuth salts of vanadic acid in several minerals. Vanadium changes its valence or capacity for holding different amounts of oxygen very readily and on account of this the dioxide has found a very important application in the manufacture of aniline black, where it acts as a carrier of oxygen or strong oxidizing agent. The dioxide becomes pentoxide, which is in turn readily reduced by giving up its oxygen to the aniline compound undergoing oxidation. One part of the dioxide in presence of potassium chlorate is able to convert 1,000 parts of aniline hydrochloride into aniline black.

COLUMBIUM AND TANTALUM.

These are two very rare metals which occur usually together in isomorphous minerals known as columbite and tantalite. The first is often called niobium.

ANTIMONY.

Occurrence. This important metal is found in nature mainly as the sulphide, or *stibnite,* Sb_2S_3. Native anti-

mony occurs in small quantities, and in many silver, lead and copper ores the metal is found in combination, usually as sulphide.

History. The gray ore or stibnite has been used since a remote period for the painting of the eyebrows, as described by Hebrew and Greek writers. The separation of the metal was first described in the fifteenth century, and because of certain virtues it was supposed to possess was very thoroughly studied. Antimony played an important part in the search for the philosopher's stone and in the attempts at transmutation of metals.

Metallurgy. Two processes are in use for the production of the metal. In one the ore is roasted to form the oxide, Sb_2O_3, which is reduced then by heating with carbon:

$$Sb_2O_3 + 3C = 2Sb + 3CO$$

In the second process the sulphide is melted in plumbago crucibles with scrap iron. A slag of ferrous sulphide separates from the reduced heavier metallic antimony. Sometimes the ore is melted in crucibles with a mixture of ferric oxide and charcoal, which accomplishes the same result. Metallic antimony is produced in Germany, Austria and Hungary, France, Italy and the United States. The production of this country in 1904 was about 2,700 metric tons of the crude metal, mostly from foreign ores. The world's production was about 18,000 metric tons in 1902.

Properties. Antimony is a light colored crystalline and very brittle metal which does not oxidize at ordinary temperatures, but which combines easily with chlorine or bromine. When heated it burns in the air. When heated with nitric acid it becomes oxidized to pentoxide. Cold, dilute hydrochloric and sulphuric acids have but little action on it. It combines readily with several metals, forming valuable alloys.

Uses. It is employed in making a few compounds, but principally in the production of several alloys. Com-

mon type metal is an alloy of about 4 parts of lead to 1 of antimony. Some very hard type metals contain 50 parts of lead, 25 parts of antimony and 25 parts of tin. Britannia metal contains 80 parts or more of tin, 10 to 15 of antimony and small amounts of zinc or copper. White metal, used for bearings, contains 80 to 90 parts of tin, 7 to 15 of antimony and 2 to 10 of copper. Babbitt metal contains tin, lead, antimony and copper in different proportions for different purposes.

Antimony Oxides. Three of these bodies are known, Sb_2O_3, Sb_2O_4 and Sb_2O_5. The first is formed by oxidizing antimony with dilute nitric acid or by decomposing the chloride by a solution of sodium carbonate:

$$2SbCl_3 + 3Na_2CO_3 = Sb_2O_3 + 6NaCl + 3CO_2$$

It is a white powder insoluble in water but soluble in hydrochloric acid and forming $SbCl_3$. This oxide also dissolves in a solution of cream of tartar, yielding potassium-antimony tartrate, $2(KSbOC_4H_4O_6).H_2O$, or tartar emetic.

The tetroxide, Sb_2O_4, is formed by heating either the trioxide or pentoxide in the air; one takes up oxygen, the other loses. This oxide is therefore the most stable of the three. The formula is often written SbO_2, and the name dioxide applied to it. The pentoxide, Sb_2O_5, is made by oxidizing the metal with strong nitric acid. It is a light yellow powder, only slightly soluble in water, but which behaves as an acid anhydride with alkalies. When fused with the latter it yields antimonates. From some of these salts antimonic acid, $HSbO_3$, may be separated as a white powder, but slightly soluble in water. The resemblance of antimony compounds to those of phosphorus is shown by the following formulas:

HPO_3	$HSbO_3$	$NaSbO_3$	NH_4SbO_3	$KSbO_3$
H_3PO_4	H_3SbO_4			
$H_4P_2O_7$	$H_4Sb_2O_7$	$H_2Na_2Sb_2O_7$	$(NH_4)_4Sb_2O_7$	$K_4Sb_2O_7$

The salt $H_2Na_2Sb_2O_7$, or acid sodium pyroantimonate,

is the most insoluble salt of this metal known and is obtained in analytical chemistry as a precipitate in the detection of sodium.

Antimony Sulphides. The trisulphide, Sb_2S_3, and the pentasulphide, Sb_2S_5, are known. The first occurs in nature as stibnite, and may be made by precipitation of a solution of antimony trichloride by H_2S. So obtained it is orange yellow and amorphous. This sulphide dissolves in an excess of hydrochloric acid and is soluble also in alkali sulphides forming sulphantimonites:

$$3(NH_4)_2S + Sb_2S_3 = 2(NH_4)_3SbS_3$$

This reaction is of great importance in analytical chemistry.

The pentasulphide, Sb_2S_5, is a dark orange precipitate formed by adding hydrogen sulphide to a solution of the pentachloride. It dissolves in alkali sulphides to form sulphantimonates:

$$Sb_2S_5 + 6NaSH = 2Na_3SbS_4 + 3H_2S$$

The salt $Na_3SbS_4.9H_2O$ is known as Schlippe's salt. The pentasulphide is prepared in quantity by boiling a mixture of powdered stibnite, sulphur and caustic soda and decomposing the Na_3SbS_4 formed by means of hydrochloric acid. It is employed in vulcanizing rubber. Several oxysulphides of antimony are known, which at one time were largely used in medicine.

Antimony Chlorides. The trichloride, $SbCl_3$, is formed as a soft mass by passing chlorine over antimony, the metal being in excess. This chloride melts easily and boils at 220°. With water it decomposes, yielding a white precipitate, SbOCl, known as the *powder of Algaroth.*

The pentachloride, $SbCl_5$, is a colorless liquid obtained by passing chlorine in excess over antimony. When heated it decomposes into the trichloride and free chlorine. The behavior of the metal with chlorine has been illustrated in an earlier chapter.

Antimony and Hydrogen. The hydride, SbH_3, a gaseous body, is easily formed by the action of nascent hydrogen on antimony compounds. The method employed for the preparation of the analogous arsenic compound, AsH_3, described in Chapter X, may be used here. The antimony compound is called stibine. It yields a dark stain on porcelain very similar to that from arsenic, but this stain is not soluble in hypochlorite solutions, while that of arsenic is.

Recognition. Antimony compounds are best recognized through the formation and decomposition of SbH_3, also by the orange yellow precipitates their solutions give with hydrogen sulphide, and the solubility of these precipitates in alkalies or alkali sulphide solutions.

BISMUTH.

Occurrence. This metal is found in the native condition usually, and sometimes as the oxide, Bi_2O_3, the sulphide, Bi_2S_3, and in a few rare minerals. Mines in Saxony furnish the largest part of the metal.

History. Bismuth has been known since the thirteenth century, but was often confounded with antimony and tin. Its true nature and important properties were pointed out about the middle of the eighteenth century.

Metallurgy. The ores are roasted and melted in pots with iron and carbon, yielding a crude bismuth containing traces of other metals. To make the pure metal the crude ingots are heated over a low fire on inclined iron plates. The pure bismuth melts and flows out, leaving the impurities behind. Bismuth ores often occur mixed with cobalt ores. In such a case slag from a previous operation is added to the iron and carbon so that cobalt collects in the new slag and is worked up as smalt.

The metal is produced chiefly by two works in Saxony and by the English firm of Johnson, Matthey & Co., from Australian and Bolivian ores.

Properties. The metal is hard and very brittle, with a relatively low melting point. It has a peculiar, reddish

white color which is characteristic. At a red heat bismuth decomposes water: it combines directly with the halogens, but is acted on only slowly by hydrochloric or sulphuric acid. Nitric acid is the best solvent. It alloys with the heavy metals, being especially valuable in the production of fusible alloys.

Uses. It is mainly employed in making alloys. Rose's metal contains 2 parts of bismuth, 1 part of lead and 1 part of tin, melting at 94°. Wood's metal, melting at 61°, contains 4 parts of bismuth, 2 parts of lead, 1 part of tin and 1 part of cadmium. It is possible to make mixtures which melt at other temperatures between 65° and 150°.

These alloys are employed as soft solders and very largely in making fusible safety plugs for steam boilers, as they may be made to melt at some definite temperature corresponding to a pressure which for safety should not be exceeded. Water pipes in automatic sprinkling systems, for protection against fire, are closed with plugs with low melting points. If the pipes become warm the plugs melt and allow the water to escape in such a manner as to extinguish the fire. Fusible alloys are often employed in making type for temporary use in newspaper printing; this is possible as they expand slightly on cooling, thus giving a sharp impression.

Bismuth is used in making several compounds, which are employed as cosmetics and in medicine.

Bismuth Oxides. Four are known, Bi_2O_3, Bi_2O_5, Bi_2O_4 and Bi_2O_5. The trioxide is the most important: it is a yellowish powder and is sometimes used in making certain kinds of glass.

Halogen Compounds. $BiCl_3$, $BiBr_3$ and BiI_3 are well known. The first in pure condition is a syrupy liquid which decomposes with water yielding the oxychloride, BiOCl. The bromine and iodine compounds decompose also, but not so readily.

Bismuth Nitrates. The metal or the oxide may be dissolved in nitric acid yielding the trinitrate, $Bi(NO_3)_3$, which may be crystallized from the acid solution. When

mixed with water this nitrate decomposes, forming a basic nitrate:

$$Bi(NO_3)_3 + 2H_2O = Bi(OH)_2NO_3 + 2HNO_3$$

This basic nitrate, or subnitrate, is an important medicinal substance.

Other Compounds. Sulphides, a basic carbonate and several chromates are among the other well known bismuth compounds. They are not important, however.

Recognition. Bismuth compounds are not stable except in presence of an excess of acid. Therefore precipitation follows when the acid solutions are mixed with a large excess of water, and this constitutes a very delicate test for them. A black sulphide is formed by precipitating a hydrochloric acid solution with hydrogen sulphide.

CHAPTER XXI.

THE CHROMIUM GROUP: CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM AND RADIUM.—RELATIONS TO THE OXYGEN GROUP.

GENERAL CHARACTERISTICS.

These elements form the primary and secondary groups of the sixth family in the Periodic System. In some respects the two groups show little in common, while from other standpoints many important likenesses may be discovered, some of which will be shown below. The elements will first be arranged in the order of their atomic weights in tabular form.

	Atomic Weight	Specific Gravity	Atomic Volume	Melting Point.	Boiling Point
Oxygen	16.00	.....	.....	.....	—180°
Sulphur	32.06	2.05	15.7	114°	440°
Chromium	52.10	6.7	7.7	high	.....
Selenium	79.20	4.60	17.2	217°	665°
Molybdenum	96.0	9.1	10.5	high	.....
Tellurium	127.6	6.25	20.4	500°	above 1,000°
Tungsten	184.00	19.1	9.7	high	.....
Uranium	238.5	18.7	12.8	high	.....

Sulphur, selenium and tellurium are distinctly non-metallic elements, and this is shown in most of their compounds. In physical behavior chromium, molybdenum, tungsten and uranium are characteristically metallic and in some of their compounds this is plainly shown. In most of them, however, the acid character is very pronounced. As metals, chromium and uranium form a number of important salts, while tungsten and molybdenum are important in the compounds they form with

metals. The elements of this family form acid oxides of the type SO_3, to which acids and well-known salts correspond.

SO_3	H_2SO_4	CrO_3	H_2CrO_4
(SeO_3)	H_2SeO_4	MoO_3	H_2MoO_4
TeO_3	H_2TeO_4	WO_3	H_2WO_4
		UO_3	(H_2UO_4)

CHROMIUM.

Occurrence. The metal is found principally as chrome ironstone, $Cr_2O_3.FeO$. It also occurs in lead chromate or crocoisite, $PbCrO_4$. In traces it occurs in several minerals, to which it imparts color, the emerald, for illustration.

History and Preparation. It was discovered in 1797 in the investigation of lead chromate, and in the same year its presence was recognized in the mineral called chrome ironstone. The separation of the metal is somewhat difficult. It has been made by the reduction of the oxide, Cr_2O_3, at a very high temperature by aid of carbon, and also by action of metallic sodium on the chloride, $CrCl_3$, at a high temperature. It may also be made by the action of aluminum on oxide of chromium as referred to some pages back. The amount of chromium produced at the present time is quite small.

Properties and Uses. Chromium is a bright, light colored metal, extremely hard and very difficult to fuse. It forms a hard alloy with iron known as chrome steel, which possesses very valuable properties, and which may find important applications in the future when methods of producing it are better understood.

Chromium Oxides. Several are known, of which the sesquioxide, Cr_2O_3, and the trioxide, CrO_3, are important. The sesquioxide is known as *chrome green*, and is made by igniting the hydroxide described below, or by strongly heating a mixture of potassium dichromate, sodium carbonate and ammonium chloride. On extracting the mass

formed with water the green oxide is left. It is used as a valuable pigment.

The formation of the green oxide is shown by this experiment:

Experiment 170. Mix 10 Gm. of powdered potassium dichromate with an equal weight of ammonium chloride and a gram of dry sodium carbonate. Rub the mixture in a mortar and then partly fill a test-tube with it. Heat the test-tube to a high temperature until the whole mass appears dark green. Then dip the tube in cold water in a beaker. This breaks the glass and allows the contents to mix with the water. The green oxide remains suspended while the other matters go into solution. This reaction amounts to a reduction of the dichromate.

The trioxide, CrO_3, is made in the form of bright red needles by the action of strong sulphuric acid on potassium dichromate. It is often spoken of as chromic acid or chromic anhydride, and is employed because of its strong oxidizing properties. It is used in laboratories on this account, in place of the dichromate which acts in a similar manner, as will be shown below.

Chromium Hydroxides. Of these the best known is the compound $Cr(OH)_3$ made by precipitating a chromic salt with ammonia water. It is a bulky, greenish blue precipitate, which when dried and ignited yields Cr_2O_3.

Halogen Compounds. The chloride, $CrCl_3$, is the most important. It may be made by passing a current of dry chlorine over a mixture of the oxide, Cr_2O_3, and carbon, and appears in the form of pinkish scales. A solution of the chloride is best made by boiling the trioxide with hydrochloric acid. A dark red, fuming liquid, known as chromium oxychloride, CrO_2Cl_2, is made by distilling a mixture of potassium dichromate, sulphuric acid and common salt. It boils at 118° and is decomposed on contact with water.

Chrome Alum, or chromium-potassium sulphate, $KCr(SO_4)_2 + 12H_2O$, is a very common substance made from potassium dichromate. At the present time it is produced in great quantities as a by-product in certain industries in which the dichromate is employed as an

oxidizing agent. An illustration will be given of this in the following experiment, in which alcohol is converted into a body known as acetic aldehyde, by oxidation:

Experiment 171. Dissolve 15 Gm. of potassium dichromate in 50 Cc. of water and add about 13 to 15 Cc. of strong sulphuric acid. Cool the mixture, and pour into it 10 Cc. of alcohol. The color changes from red to dark violet or olive green; and a vapor, with a sharp, characteristic odor, escapes. This is aldehyde. Allow the liquid to evaporate spontaneously, which will require several days, and observe the crystals of chrome alum formed.

The color of the solution of chrome alum depends on its temperature. If made at a low temperature it is dark violet, but this turns to green by application of heat, from the formation of complex salts in which the chromium and acid are differently united.

The reaction in the above experiment appears complex, but may be shown to be this:

$$K_2Cr_2O_7 + 4H_2SO_4 + 3C_2H_6O + 24H_2O = 2(KCr(SO_4)_2.12H_2O) + 3C_2H_4O + 7H_2O$$

Each molecule of alcohol has lost two atoms of hydrogen, and this hydrogen, plus that from the sulphuric acid, has been taken by the seven atoms of oxygen in the dichromate to form seven molecules of water.

A solution of chrome alum yields a precipitate with ammonia water, this precipitate consisting of chromium hydroxide, $Cr(OH)_3$, while a solution of the dichromate yields no precipitate with alkalies, but changes color from formation of chromate, as the following equations illustrate:

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O$$

$$2KCr(SO_4)_2 + 6NH_4OH = 2Cr(OH)_3 + K_2SO_4 + 3(NH_4)_2SO_4$$

The Chromates. These are the compounds of chromium trioxide, and include several extremely important substances of which sodium and potassium dichromates are the best known. These are prepared indirectly from

chrome ironstone. The ore is ground and heated to a high temperature with lime or chalk, the mass being well stirred to give the air access.

$$4Cr_2O_3FeO + 7O_2 + 8CaCO_3 = 8CaCrO_4 + 8CO_2 + 2Fe_2O_3$$

The cool mass is then extracted with water and the calcium chromate solution thus obtained is converted into the sodium or potassium compound by double decomposition with an alkali sulphate. The alkali chromates are in turn treated with acid to form dichromates, which being less soluble may be more easily purified by crystallization:

$$2Na_2CrO_4 + 2HCl = Na_2Cr_2O_7 + H_2O + 2NaCl$$

Solutions of the chromates are yellow, while those of the dichromates are reddish yellow. Potassium dichromate was for a long time the most important salt of the class, but at the present time the corresponding sodium compound is very largely used, because of its greater solubility. The chromates of the heavy metals are insoluble precipitates. Lead chromate, $PbCrO_4$, is known as *chrome yellow*, and is made by precipitating a solution of the dichromate with lead acetate. *Chrome orange* is a basic lead chromate, $PbCrO_4.Pb(OH)_2$, made by precipitating an alkaline chromate by a soluble lead salt. Both lead chromates are used in dyeing. *Silver chromate*, Ag_2CrO_4, is a deep red precipitate formed on addition of a chromate to silver nitrate solution. *Barium chromate* appears as a yellowish precipitate on mixing chromate solutions with those of soluble barium compounds.

Recognition. Salts in which the chromium acts as the metal are usually pink or violet and give down the chromium in the form of hydroxide on addition of ammonia. These compounds when fused with alkaline oxidizing agents are converted into yellow salts of chromic acid. These salts yield the precipitates with lead and barium compounds mentioned above.

MOLYBDENUM.

This is a comparatively rare metal found mainly in the disulphide, MoS_2, and in a lead combination, $PbMoO_4$. The free metal has no technical uses. An important compound, the trioxide, MoO_3, is made from the sulphide by oxidizing it in the air. This trioxide is technically called molybdic acid. It forms salts called molybdates, of which ammonium molybdate, $(NH_4)_2MoO_4$, is the most important. This molybdate is a useful laboratory reagent, being employed in the detection of phosphorus in phosphates. Molybdic acid forms very complex salts, and the commercial ammonium salt has a formula which is usually given as $(NH_4)_6Mo_7O_{24}.24H_2O$.

A solution of the trioxide in sulphuric acid is a common reagent employed in the detection of alkaloids.

TUNGSTEN.

This metal is found commonly in wolframite, $FeWO_4$, and scheelite, $CaWO_4$, and also in several rarer minerals. The metal may be obtained by reduction of the oxides by hydrogen, and also by the general aluminum reduction process, but has few applications in the arts. It is sometimes combined with iron to form a kind of steel. One of the most important compounds is the trioxide, WO_3, which is often called tungstic acid. It may be obtained by decomposing a tungstate with an acid as a bulky precipitate which yields a yellow powder on drying. Sodium tungstate may be made from the native wolframite by fusing the latter with a mixture of sodium carbonate and nitrate. The fused mass is leached with water and the solution so obtained is evaporated to crystallization. The crystals have not the simple formula Na_2WO_4, but are much more complex, resembling in this respect those of molybdic acid. The common commercial sodium tungstate is $Na_{10}W_{12}O_{41}$ with $21H_2O$ to $28H_2O$, the amount of water depending on the temperature of crystallization. A solution of this salt is used as a mordant in dyeing and also in impregnating muslin to render it uninflammable. It is employed in the preparation of several reagents for laboratory purposes.

Wolfram Bronzes. A very peculiar class of compounds is obtained by the partial reduction of tungstates by heating in hydrogen, illuminating gas, or with certain metals. From their colors and physical properties these bodies are called wolfram or tungsten bronzes. Potassium-tungsten bronze is a purple blue powder, having the formula $K_2W_4O_{12}$. A yellow sodium-tungsten bronze has the formula $Na_5W_6O_{18}$; a blue bronze the formula $Na_2W_5O_{15}$, and a purple red bronze the formula $Na_2W_8O_9$. These are combinations of varying amounts of WO_3 with alkali, and are practically used as bronze paints for many purposes. Many complex compounds of tungstic acid with boric and phosphoric acids are known, but they have no technical importance.

URANIUM.

This rare metal is found in a few ores, the most important being a complex oxide known as *pitch-blende*. The free element may be obtained as a steel white substance by reducing one of the chlorides with sodium. By fusing pitch-blende with a mixture of sodium carbonate and nitrate a soluble sodium uranate, $Na_2U_2O_7$, is obtained, which is known as uranium yellow and which is employed in coloring glass. By double decomposition with ammonium chloride this salt yields the ammonium compound, which is decomposed by heat with formation of the oxides UO_2 and UO_3. From this mixture several other uranium compounds may be made. The most important of these is the nitrate, $UO_2(NO_3)_2.6H_2O$, which is obtained in beautiful yellow fluorescent crystals. A solution of this salt or the corresponding acetate is often employed in the laboratory for the determination of phosphates.

In the formation of salts uranium seems to act with a valence of four and six, giving rise to the uranous and uranic compounds. As illustrations of the uranous compounds we have the dioxide, UO_2, the tetrachloride, UCl_4, and the sulphate, $U(SO_4)_2$. Among the uranic compounds we have the trioxide, UO_3 or $(UO_2)O$, the group (UO_2) being called uranyl; the chloride or

uranyl chloride, UO_2Cl_2, uranyl sulphate, $UO_2(SO_4).3H_2O$, and nitrate referred to above, $UO_2(NO_3)_2.6H_2O$. These uranic compounds may be regarded as containing the group (UO_2).

RADIUM.

In the examination of certain uranium salts H. Becquerel in 1896 discovered a new kind of light ray which has the power of passing through opaque bodies and acting on sensitive photographic plates. In studying the matter further it was found that even more strongly active substances could be obtained from the pitch-blende minerals used in making the uranium salts. It was concluded that these minerals must contain some new element on the presence of which this peculiar property depends, and Professor and Madame Curie finally succeeded in separating a substance which is evidently the new element, to which they gave the name radium. The atomic weight of the element is about 225, as found from the radium chloride. In the periodic arrangement of the elements it would fall under barium and in the horizontal row with uranium and thorium.

The radium salts are phosphorescent and have the power of imparting this property to other bodies to some extent. Apparently three kinds of rays are given off from radium compounds; heat energy is also liberated and at the rate of about 100 calories per hour for 1 gram of pure radium. No simple explanation has been yet given for this very remarkable fact. In addition to the three kinds of rays and the heat energy, radium gives off, also, a so-called *emanation* at an elevated temperature. This emanation is a gaseous substance which may be condensed at a very low temperature. It is strongly radio-active and in turn suffers itself decomposition, yielding helium as one of the products.

The radium rays possess marked physiological as well as chemical and physical action, but from the mass of conflicting statements now current it is not possible to deduce simple laws, which may be properly presented in an elementary book.

CHAPTER XXII.

MANGANESE AND ITS RELATIONS TO THE HALOGEN GROUP.

GENERAL CHARACTERISTICS.

In the seventh family of the Periodic System there are two groups which appear to have but little in common. In the primary group we find manganese alone, and in the secondary group the halogen elements already described. In many respects manganese resembles iron and in some of the salts a resemblance is found. But there are other considerations which justify the grouping of this metallic element with such pronounced non-metals as chlorine and bromine. Like chromium and other elements described in the last few chapters, manganese forms two classes of compounds. In some it acts as a metal, while in others it behaves as the acid element. It is among these compounds that we must look for the analogies with the chlorine group. Manganese forms at least five oxides, the highest one of which is Mn_2O_7. This with water yields an acid with the strongest oxidizing properties, and having the composition $HMnO_4$. The halogen oxides of the type X_2O_7 are not known but the acids corresponding are, and also salts. We have

	$HMnO_4$	$KMnO_4$	$Ba(ClO_4)_2$
	$HClO_4$	$KClO_4$	$Ba(BrO_4)_2$
	$HBrO_4$	$KBrO_4$	$Ba(IO_4)_2$
Mn_2O_7	HIO_4	KIO_4	$Ba(MnO_4)_2$

All of these acids may be looked upon as related to the oxide in this way:

$$X_2O_7 + H_2O = 2HXO_4$$

The most important compound of manganese is the

salt $KMnO_4$. This is isomorphous with the perchlorate, with which it will crystallize in all proportions. In connection with somewhat analogous chemical behavior this relation is important in suggesting the place of manganese among the elements. On the other hand, as will appear below, manganese forms salts which in structure resemble the chromates. Thus we have Na_2MnO_4, as we have Na_2CrO_4, but the manganate is far less stable than is the chromate, and the corresponding oxide, MnO_3, is known only as a compound of little stability.

Occurrence. Manganese is found principally in the dioxide known as pyrolusite, MnO_2, in braunite, Mn_2O_3, in hausmannite, Mn_3O_4, and in sulphides and rarer ores. Many iron ores contain traces of manganese.

Preparation and Properties. Pure manganese has not been readily obtained, but may be produced as is iron by blast furnace reduction, employing a higher temperature and more carbon. This yields a cast manganese containing carbon. But a much better product is made by reducing one of the oxides by means of aluminum. This, it will be recalled, is a general process for many metals. The pure metal is also made on a small scale by reduction of the chloride with sodium or magnesium, and by several other processes.

The atomic weight of manganese is 55.0, the specific gravity about 8, with the atomic volume, therefore, 6.9. The pure metal is very hard and may be melted only at a high temperature. It oxidizes very readily in the air and decomposes water at a relatively low temperature.

Uses. In pure form the metal has no technical applications. Several alloys are important, one being used in the production of Bessemer steel.

Manganese Oxides. At least ten of these combinations have been described, but not over five are thoroughly well known. *Manganous oxide,* MnO, is a greenish or gray powder obtained by the reduction of the other oxides in a current of hydrogen. It dissolves in acids forming manganous salts. *Manganic oxide,* Mn_2O_3, is found in nature as braunite, and may be prepared artifi-

cially also. In composition it corresponds to chromic oxide, Cr_2O_3, and ferric oxide, Fe_2O_3. With acids it yields manganic salts, as $MnCl_3$ and $Mn_2(SO_4)_3$. *Manganous-manganic oxide*, Mn_3O_4, occurs as hausmannite, and may be made by heating the dioxide to a high temperature.

The *dioxide*, MnO_2, is the best known and by far the most important of the manganese oxides. It is found as pyrolusite in many parts of the world and has several technical uses. It is employed with potassium chlorate in the manufacture of oxygen; it is used for the decomposition of hydrochloric acid in the chlorine industry, and is used in immense quantities in the production of spiegeleisen for the Bessemer steel industry. It is also employed in considerable quantities for the production of colorless glass from common materials which contain iron. When heated to a high temperature it gives up one third of its oxygen:

$$3MnO_2 = Mn_3O_4 + O_2$$

The *trioxide*, MnO_3, has been described, but it is not stable or important. The same may be said of several others. The *heptoxide*, Mn_2O_7, is obtained as a dark-green liquid by the action of sulphuric acid on potassium permanganate. This liquid is somewhat volatile and decomposes easily with explosive violence. With organic substances it unites immediately with explosive oxidation. With water it yields permanganic acid, as explained above.

Manganese Hydroxides. Several are known, but they have little importance. *Manganous hydroxide*, $Mn(OH)_2$, is obtained by precipitating manganous salts with alkali hydroxides. It is a light colored, flocculent precipitate which soon oxidizes in the air to higher hydroxides, with dark color.

Manganese Chlorides. The most important one of these is the well-known pink salt $MnCl_2.4H_2O$, which may be obtained by the solution of manganese or its sulphide in hydrochloric acid, or as a by-product in the chlorine industry from MnO_2. The salt is very soluble

in water and may be crystallized with different amounts under special conditions.

In the production of chlorine from hydrochloric acid and manganese dioxide it is commonly assumed that the reaction takes place between the two substances in this way:

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$

It is likely however, that other chlorides are formed in the operation to be subsequently decomposed in this manner:

$$MnCl_4 = MnCl_2 + Cl_2$$

The trichloride, $MnCl_3$, is probably formed also when the acid is cold and strong, but both this and the tetrachloride break up readily, liberating chlorine and leaving the dichloride.

$MnBr_2$ and MnI_2 are salts corresponding to manganous chloride, but they are not important.

Manganese Sulphates. The most important is the *manganous sulphate,* $MnSO_4$, which may be obtained crystallized with 3, 4, 5 or $7H_2O$, the amount of water held depending on the concentration and temperature of the crystallizing solution. Manganous sulphate and the alkali sulphates crystallize together. *Manganic sulphate,* $Mn_2(SO_4)_3$, is known, but its solution is not very stable. With alkali sulphate solutions it yields alums, but they are not very stable.

Many other compounds of metallic manganese, a sulphide, MnS, a carbonate, $MnCO_3$, a nitrate, $Mn(NO_3)_2$, etc., are known, but they are not practically valuable. The most important combinations of manganese are those in which it exists in highly oxidized or acid condition, as in the manganates and permanganates.

Potassium Permanganate. This important salt, which consists of deep purple crystals, may be looked upon as the potassium compound of permanganic acid, in turn derived from the heptoxide, Mn_2O_7:

$$2KOH + Mn_2O_7 = 2KMnO_4 + H_2O$$

Practically, the salt is produced by a very different reaction. Manganese dioxide in powder is heated with a mixture of potassium hydroxide and an oxidizer, either the nitrate or chlorate, which gives rise to a green salt, the *manganate*, K_2MnO_4:

$$3MnO_2 + 6KOH + KClO_3 = 3K_2MnO_4 + 3H_2O + KCl$$

By lixiviating with water and passing CO_2 into the solution this crude manganate is decomposed with formation of permanganate and other products:

$$3K_2MnO_4 + 2CO_2 = 2K_2CO_3 + 2KMnO_4 + MnO_2$$

The purple solution is filtered from the precipitated dioxide through marble dust and is concentrated to the point where crystallization takes place. As the salt is not very soluble in cold water it is easily made pure in this way. By using chlorine the whole of the manganate may be saved as permanganate, and this is done on the technical scale:

$$2K_2MnO_4 + Cl_2 = 2KMnO_4 + 2KCl$$

A crude permanganate of sodium or potassium is made by treating the corresponding crude manganate solution with a little dilute sulphuric acid. The solution so obtained has been used directly in large quantities in the oxidation of sewage and for similar purposes.

Practically all the uses of the permanganate depend on its power of readily liberating oxygen, and because of this behavior it is largely used in technical and analytical chemistry.

In acid solution the permanganate behaves as an oxidizing agent, as illustrated in the following equations:

$$2KMnO_4 + 5C_2O_4H_2 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$

In this case oxalic acid is oxidized to water and carbon dioxide, and as the reaction is a perfectly sharp and

definite one a valuable process of quantitative volumetric analysis is based on it. The next equation illustrates the use of the permanganate in another volumetric process, where ferrous iron is oxidized to ferric iron:

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

These changes depend on the fact that two molecules of the permanganate with acid liberate five atoms of oxygen:

$$2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 3H_2O + 5O$$

In several very important practical cases the permanganate is used as an oxidizer in neutral or alkaline solution, but the reaction is then a different one, and may be illustrated as follows:

$$2KMnO_4 + H_2O = 3O + 2KOH + 2MnO_2$$

If the solution is sufficiently alkaline to begin with the MnO_2 does not precipitate, but dissolves to form a manganite. In this case two molecules of permanganate give up three atoms of oxygen instead of five. When the student takes up the subject of volumetric analysis the high importance of all these reactions will be recognized. The reactions with sulphurous acid and hydrogen dioxide referred to in former chapters take place according to these equations:

$$2KMnO_4 + 5H_2SO_3 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5H_2SO_4 + 3H_2O$$

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

Recognition. The salts and oxides of manganese become converted into manganates when fused with an alkali and a little potassium chlorate. The green color is characteristic. The formation of a flesh colored precipitate of sulphide when a manganous salt is treated with ammonium sulphide solution is also characteristic.

CHAPTER XXIII.

THE IRON GROUP: IRON, NICKEL AND COBALT.

GENERAL CHARACTERISTICS.

These three elements form a natural period in the eighth family of the Periodic System. They resemble each other as metals and also in the character of many of their compounds. Thus, they form similar sulphates and double sulphates with members of the alkali group. They form oxides of the types MO and M_2O_3. From another standpoint, however, they may be looked upon as forming a gradual transition between manganese in the seventh family and copper in the first.

Because of the closeness of their atomic weights the proper classification of these metals is a matter of some uncertainty. It is even held by several chemists that cobalt and nickel are not true elements, but mixtures of metals yet to be separated. This question is one which cannot be discussed in a book for beginners. Accepting the usual views, the following table shows the important physical constants of the group:

	Atomic Weight.	Specific Gravity.	Atomic Volume.	Melting Point.
Iron	55.9	7.8	7.2	1800°
Nickel	58.7	8.9	6.6	1500°
Cobalt	59.0	8.6	6.8	1800°

In the properties of the metals and their common salts cobalt stands between iron and nickel.

IRON.

Occurrence. Metallic iron is occasionally found as a natural substance, but in this form it is quite unimportant. It is relatively abundant and widely distributed in a number of minerals, of which the oxides, sulphide and carbonate are technically valuable. The natural oxides which are important are hematite, Fe_2O_3, which occurs in varieties known as specular iron ore, micaceous ore, red ochre and others; limonite, $Fe_2O_3 +$ water, of which brown hematite, bog iron ore and yellow ochre are varieties; magnetite, Fe_3O_4, or the magnetic oxide of iron. Franklinite is a ferric oxide in which some of the iron is replaced by zinc. Ferrous carbonate, $FeCO_3$, occurs as spathic iron ore; an impure variety is known as clay ironstone. The native sulphide of iron, FeS_2, is known as iron pyrite and is valuable for its sulphur rather than for its iron.

History. The metal has been used from the earliest historical times. Ores were reduced by the ancient Hebrews, Egyptians, Greeks and Romans by methods which were doubtless very crude. In China and India the metal was apparently known at a remote period. After their conquest of Britain the Romans began working deposits of iron in localities which still yield the ore in quantity. The history of improvements in the smelting of ores on the large scale is obscure, but the greatest advance was made in the introduction of the blast furnace, which was probably as late as the sixteenth century. With the recognition of the chemical differences between cast iron, wrought iron and steel, the development of a rational metallurgy of iron became possible, and since the middle of the eighteenth century great advances have been made in all civilized nations in the smelting and working of the metal.

Metallurgy. The oxides, or carbonate yielding oxide, are the only ores of importance for the production of metallic iron. The reduction of the oxide to the state of metal depends on the behavior with carbon monoxide at a high temperature; like carbon itself this body is a strong

reducing agent under proper conditions, and with ferric oxide brings about this change:

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2$$

Blast Furnace.

The smelting of iron ores is carried out in a blast furnace, the general arrangement of which is shown in the accompanying figure.

Such furnaces are from 60 to 100 feet high and from 15 to 20 feet wide in the widest part. At the bottom of the furnace there are openings, called tuyères, through which a blast of heated air may be blown in under considerable pressure. After being thoroughly heated by combustion of fuel the furnace is charged with alternate layers of coke (charcoal or anthracite is sometimes used), ore and limestone to the top. The oxygen of the blast forms CO_2 at the base of the furnace, but this becomes reduced to CO by the excess of carbon a short distance higher. This CO in turn acts on the oxide of iron, reducing it as explained above. The reduced iron gradually settles down in the furnace and finally melts, collecting at last in the liquid condition in a kind of hearth at the bottom. Meanwhile more ore, fuel and limestone are added at the top, the process being kept up continuously. From time to time, usually every eight or twelve hours, the hearth below is tapped by withdrawing a plug and the molten iron collected is allowed to run out into trenches made in sand of the casting floor in front of the furnace. The iron soon solidifies in the form of rough bars, which are technically called "pigs." This pig iron is essentially what is known as cast iron, the nature of which will be soon explained.

As all ores contain certain earthy matters it is necessary to add something to the charge in the furnaces to separate these in the form of a slag. Limestone is usually added because the impurities are commonly silicates. The limestone is called a flux, as it forms with the silicate an impure calcium silicate which separates as a slag or glass and collects finally as a liquid layer just

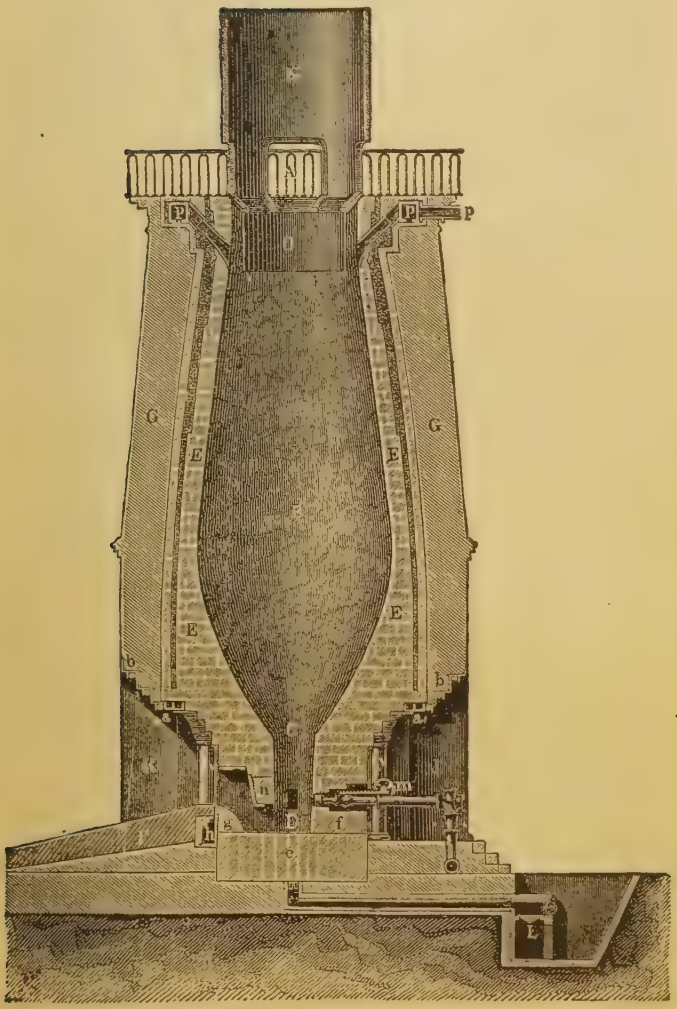

FIG. 32.

above the molten iron. Through an opening above that for the iron, this slag is run off from time to time. In settling down toward the hearth of the furnace, the soft, spongy reduced iron takes up carbon, which assists greatly in bringing it finally into the molten condition. The pig iron formed is therefore a combination of iron with carbon, which melts much more readily than pure iron.

Blast furnaces were formerly open at the top, permitting the waste gases and products of the combustion and reduction to escape. At present, as the illustration shows, the top is closed and the gases are led down through a large pipe from which they are conveyed to a furnace and burned to heat the air blast forced in through the tuyères. This exit pipe is shown at p, and the entrance of one of the tuyères at m.

Practically, three varieties of iron are recognized, viz.: *cast iron, wrought iron* and *steel.*

Cast or Pig Iron is characterized by containing several per cent of foreign substances, of which carbon is essential and by far the most important. Traces of sulphur, phosphorus, silicon and manganese are always present. The first two in more than very minute traces are very objectionable, as they render the iron brittle. Carbon exists in cast iron in two forms known as combined carbon and graphitic carbon. In cast iron with a gray fracture the graphite carbon predominates. When such iron is dissolved in acids the carbon is left in the free condition. Cast iron in which the carbon is in chemical combination has a white fracture. This iron dissolves in acids with evolution of hydrocarbon gases having a peculiar characteristic odor. This carbon exists in the iron as carbide, or carbides, as there are doubtless several combinations. These may be broken up by water or steam at a high temperature just as calcium carbide is decomposed by water at the ordinary temperature. Cast iron is employed practically because it may be melted at a relatively low temperature and poured into molds.

Wrought Iron was formerly produced almost wholly from pig iron by the operation known as puddling. The pigs are melted on the hearth of a reverberatory furnace, the hearth being often lined with oxide of iron. The oxygen of the air passing over the metal, with that from the hearth, gradually burns out the carbon to form CO, while the silicon, phosphorus and sulphur become oxidized and with a little of the iron form a slag. These operations are assisted by puddling or stirring the melted metal. As the refining progresses the iron becomes thick and pasty; it is then worked into a ball, withdrawn from the furnace and hammered and rolled to squeeze out the slag impurities. To further improve it, it is reheated in a furnace and rerolled, this operation being in some cases repeated several times. By such treatment the metal is given a fibrous structure, greatly increasing its strength and tenacity. At the present time a product of the same character is made by the Bessemer process to be described. Wrought iron is as nearly pure iron as can be made. It often contains 99.5 per cent of real iron, the rest being made up of traces of several impurities, and is characterized by being malleable, ductile and easily welded. It requires a very high temperature for melting.

Steel is chemically a product between pure wrought iron and cast iron, as it always holds a certain small amount of carbon in combination. The proportion of carbon varies in different kinds of steel between 0.15 per cent and 1.5 per cent, and between soft steel and wrought iron no real difference exists. Several methods are in use for the production of steel. In one process bars of wrought iron are heated in contact with powdered charcoal, by which means carbon is absorbed and combined, producing what is known as *blister* steel, from the appearance of the bars at the end of the heating. This is melted in a plumbago crucible, forming a much more uniform mass, which is poured into molds forming *crucible steel* or *cast steel*. This is employed for many purposes. At the present time the largest quantities of steel are made directly from pig iron by the *Bessemer process*, or by the *Siemens open hearth process*.

Bessemer Steel is made from pig metal by a series of comparatively simple operations. This pig iron is melted in a furnace and run into a vessel called a converter, which is furnished with a perforated bottom and tight air chamber below. Through the perforations air is blown under considerable pressure into the molten metal. It speedily unites with and burns out practically all of the carbon, leaving a liquid mass corresponding to wrought iron. Into this is run a known weight of melted spiegeleisen, which is a cast iron containing manganese and very rich in carbon. The proportion of carbon in this having been determined by previous analysis, it is possible to take enough of it to produce with the iron in the converter a steel of the desired composition. The manganese leaves the iron and goes into the slag always formed in the operation. The converter employed is usually a pear shaped vessel, built of iron plates and lined with a silicious material called ganister, for some kinds of pig metal, or with a mixture of lime and magnesia for metal rich in phosphorus. It is made to rotate on trunnions so that it may be tipped to receive the charges, and again at the end of the operation to pour out the finished steel. As much as fifteen to twenty tons of pig iron may be taken as a charge and converted into steel in half an hour in one of these converters. Bessemer steel has displaced wrought iron for many structural purposes.

Open Hearth Steel is made by melting pig iron along with iron oxide or scrap iron in the hearth of a kind of reverberatory furnace resembling a puddling furnace. The pig iron becomes decarbonized to the right extent by properly conducting the operation. In these furnaces a gaseous fuel must be used, and this may be obtained in a simple manner from coal, or from other source. The production of steel by this method requires more time than is the case with the Bessemer process, but the quality is in general more uniform.

Malleable Iron articles are made by casting in the usual manner. They are then imbedded in powdered oxide of iron and heated to a low red heat about two days. In this manner a part of the carbon is removed

from the cast iron and the articles become soft enough and malleable enough to be worked in various ways. It will be seen that malleable iron is a cheap substitute for wrought iron.

In 1903 the world's production of pig iron was 46,733,039 metric tons, of which the United States furnished 18,297,400 metric tons, Great Britain 8,952,183 metric tons and Germany 10,085,634 metric tons. The world's production of steel, in 1903, was 35,356,355 metric tons, of which the United States furnished 14,756,691 metric tons, Great Britain about 5,114,647 metric tons, and Germany 8,801,515 metric tons. In these data steel includes wrought iron.

Properties and Uses of Iron. These are too well known to call for extended discussion here. Iron is very malleable and ductile and is a moderately good conductor of electricity. In the form of steel it takes a high temper, that is, may be hardened to almost any desired degree. Soft iron may be temporarily magnetized and very strongly, but on withdrawal of the magnetic influence the property is lost. Steel, on the other hand, becomes permanently magnetized. At a high temperature iron decomposes steam, liberating hydrogen and leaving the black oxide, Fe_3O_4. When heated to a high temperature and plunged into a jar of oxygen it combines, forming the same oxide. Iron forms two classes of compounds, ferrous and ferric. Its power of combining with other metals to form alloys is limited, but a few such combinations are known.

Iron Oxides. Three are well known. *Ferrous oxide*, FeO, is not readily prepared or kept in pure condition. It may be made by reduction of ferric oxide by hydrogen at a temperature of 300°. When exposed to air or oxygen it oxidizes immediately. *Ferric oxide*, or sesquioxide, Fe_2O_3, occurs in nature in the important ores mentioned. It is made easily by heating precipitated ferric hydroxide, or by the calcination of dried green vitriol, as in the manufacture of fuming sulphuric acid. In this form it is known as jewelers' rouge and is used for polishing.

Iron is trivalent in this and other ferric compounds. The *black oxide*, magnetic oxide, ferroso-ferric oxide, Fe_3O_4, occurs in nature as an iron ore and may be made artificially. It may be looked upon as a combination of ferrous and ferric oxide, $FeO.Fe_2O_3$. It is easily made by passing steam over red hot iron. Such a coating is often formed on iron to keep it from rusting, as in the Bower-Barff process.

The reduction of ferric oxide to metallic iron is illustrated by the following experiment:

Experiment 172. Arrange the apparatus as shown in the next figure. Generate hydrogen in the usual manner, and dry it by passing it through the bottle containing strong sulphuric acid. Charge the hard glass tube with a few grams of ferric oxide (jewelers' rouge). The outer end of the tube is closed with a perforated stopper, through which passes a narrow glass tube for the escape of the hydrogen and steam. After the apparatus

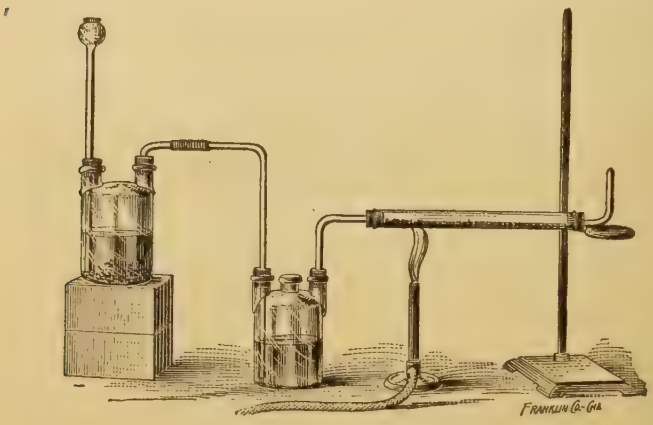

FIG. 33.

is arranged allow the gas to stream through some minutes to expel the air thoroughly. Then carefully heat the tube by a Bunsen burner, and keep hot until steam no longer escapes from the open end. Meanwhile a good current of hydrogen must continue to pass. When the reduction is complete remove the lamp, but allow the product to cool thoroughly in the stream of hydro-

gen before taking apart the apparatus. The reduced iron is left as a fine, dark gray powder, which burns readily when thrown into the flame of a Bunsen burner.

The reduction follows according to the equation:

$$Fe_2O_3 + 3H_2 = 3H_2O + 2Fe$$

When the reduction is carried out at a proper temperature, a low red heat, the powder possesses the property of burning spontaneously when thrown into the air.

Iron Hydroxides. *Ferrous hydroxide*, $Fe(OH)_2$, may be made as a greenish precipitate by adding an alkali solution to one of a ferrous salt. In absence of air the precipitate is almost white, but it oxidizes quickly, turning greenish brown. *Ferric hydroxide*, $Fe(OH)_3$, is best made by precipitating a ferric salt with ammonia water:

$$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl$$

It is reddish brown and soluble in strong solutions of ferric salts. Such a solution exists in the mixture known as dialyzed iron. A crude ferric hydroxide is often employed in purifying coal gas by absorbing sulphur compounds.

Iron Sulphides. *Ferrous sulphide*, FeS, is made by melting a mixture of sulphur and scrap iron or by precipitating a ferrous solution by means of ammonium sulphide. It is a black substance and is decomposed by acids with liberation of hydrogen sulphide. *Ferric sulphide*, FeS_2, occurs as pyrite and is valuable on account of the sulphur it contains. It is employed largely in the manufacture of sulphuric acid. The native substance is found in brassy yellow cubes or octahedra.

Iron Chlorides. *Ferrous chloride*, $FeCl_2$, may be obtained in solution by dissolving the metal in hydrochloric acid. It crystallizes with $4H_2O$ in green, very soluble crystals. The pure dry substance is made by passing hydrochloric acid gas over hot iron. *Ferric chloride*, $FeCl_3$, is obtained in solution by dissolving iron in aqua regia and repeatedly evaporating with hydrochloric acid, or by dissolving in hydrochloric acid and passing in

chlorine. It is very soluble in water and also in alcohol and ether. The anhydrous substance is obtained in the form of crystalline scales by passing chlorine gas over red hot iron. Ferric chloride is one of the most important of the iron salts.

Ferrous bromide, $FeBr_2$, and iodide, FeI_2, are well known and are employed in medicines as syrups.

The reduction of a ferric to a ferrous salt and the reverse reaction are illustrated by the following experiments:

Experiment 173. Heat a few cubic centimeters of a ferric chloride solution in a test-tube and add a little hydrochloric acid and some small fragments of zinc. A lively evolution of hydrogen follows, and the color of the solution becomes lighter. In a short time it disappears almost completely, leaving a ferrous solution with a faint green tinge. The hydrogen set free by the acid and zinc acts on the $FeCl_3$, removing part of its chlorine,

$$FeCl_3 + H = FeCl_2 + HCl$$

Experiment 174. Dissolve about 5 Gm. of green vitriol in water, in a beaker, and add 3 or 4 Cc. of dilute sulphuric acid (1 to 5) and about 10 drops of strong nitric acid. Heat the mixture to boiling in a fume closet, and observe the change of color. Red fumes escape, and when the action ceases the salt described below is left in solution.

Iron Sulphates. Crystallized *ferrous sulphate*, $FeSO_4.7H_2O$, is a common substance, known as green vitriol. It may be made by dissolving iron in dilute sulphuric acid and evaporating to crystallization, or by the oxidation of iron sulphides in moist air. The salt is very soluble in water, but not in alcohol. It is employed in the preparation of many other compounds of iron, and especially in the production of inks and pigments used in dyeing. A crude sulphate is used as a deodorizer. When carefully heated to about 140° it loses $6H_2O$ and leaves a colorless salt. The last molecule of water is expelled at a much higher heat. With ammonium sulphate it forms the important compound $(NH_4)_2SO_4FeSO_4.6H_2O$. This is much more stable than green vitriol. *Ferric sulphate*, $Fe_2(SO_4)_3$, is obtained in solution by oxidizing ferrous sulphate by aid of nitric acid after addition of more sul-

phuric acid. This solution is used in pharmacy. Ferric sulphate crystallizes with ammonium sulphate in the proper proportion, yielding *ferric alum*, $NH_4Fe(SO_4)_2 . 12H_2O$. This salt is stable in the air. A similar compound is formed with potassium sulphate.

Iron Nitrates. The *ferrous and ferric* salts are known. *Ferric nitrate*, $Fe(NO_3)_3$, is employed in making Prussian blue for dyeing.

Iron Phosphates. *Ferrous phosphate*, $Fe_3(PO_4)_2 . 8H_2O$, is formed as a light colored precipitate by precipitating a solution of ferrous sulphate with sodium phosphate. It is used in medicine. Ferric phosphates are also known.

Other Compounds. Iron is found in the important substances potassium ferrocyanide, $K_4Fe(CN)_6$, and potassium ferricyanide, $K_3Fe(CN)_6$. These may be looked upon as double cyanides, or, better, as salts of ferrocyanhydric acid and ferricyanhydric acid. They are used as valuable laboratory reagents and in the manufacture of Prussian blue and Turnbull's blue.

Recognition. The hydrated ferrous salts are usually light green. The ferric salts yield yellow to brown solutions. Ferrous salts give with ammonia light greenish ferrous hydroxide, while ferric salts give a precipitate of reddish ferric hydroxide. With potassium ferricyanide ferrous salts give a deep blue, while ferric salts yield a deep blue precipitate with potassium ferrocyanide.

NICKEL.

Occurrence. This metal occurs usually as sulphide associated with other metallic sulphides. Nickel blende, NiS, nickel glance, $Ni(AsS)_2$, and kupfer-nickel, NiAs, and a complex nickel-magnesium silicate are the most important ores.

History. Nickel has been known since 1751, when it was discovered among German ores worked for copper.

After that time the metal was found rather widely distributed and is now produced from mines in Germany, New Caledonia and Canada.

Metallurgy. The processes employed in the preparation of pure nickel from its ores are in the main complex because of the peculiar nature of the native compounds. In the simplest case the sulphide is roasted to form oxide and this is reduced with carbon in the usual manner. But as a rule much more difficult processes are necessary, and a description of them lies beyond the scope of this book. No accurate figures can be given of the production of pure nickel at the present time. In 1902 this country furnished about 4,700 tons, chiefly from Canadian ores. The world's total production was about three times that amount.

Properties. Nickel is a very hard metal which takes a high polish and corrodes in the air only superficially. It is but slowly dissolved by acids, and alkalies may be fused in contact with it without danger of much corrosion. By special treatment the metal has been made malleable and ductile, and in this form has found many uses. It alloys with several metals readily.

Uses. It is employed mainly as a coating for iron in the form of nickel plate. It is also used in making several important alloys. German silver contains copper, zinc and nickel. The 5 cent pieces of this country contain 75 parts of copper and 25 of nickel. A combination with iron known as nickel-steel is also important.

Compounds of Nickel. *The sulphate*, $NiSO_4.7H_2O$, and the *ammonium-nickel sulphate*, $(NH_4)_2Ni(SO_4)_2.6H_2O$, are the most important compounds. The latter is commonly used in nickel plating. Hydrated nickel salts are green to greenish blue, while the anhydrous salts are yellow. Many other nickel compounds are known, but they have little technical importance.

Recognition. When nickel compounds are fused in a borax bead this becomes yellowish brown. In alkaline

solution nickel compounds yield with hydrogen sulphide a black precipitate of NiS.

COBALT.

Occurrence. This metal is found often associated with nickel in arsenic or sulphur combination. Free cobalt and nickel are found in meteorites. An arsenide containing cobalt, nickel and iron, called tin-white cobalt, is the most important ore.

Metallurgy. The separation of cobalt from its ores is difficult and the industry is not an important one.

Properties and Uses. Cobalt is a white metal with a reddish tinge. It is magnetic and very hard and in the form of wire possesses great strength. It is possible to deposit cobalt as a coating on other metals as nickel is deposited, but this industry has not yet become important.

Cobalt Compounds. The hydrated salts are rose red, but when deprived of their water of crystallization they are deep blue. The monoxide, CoO, is a brownish black powder. The best known salts are the *sulphate*, $CoSO_4.7H_2O$, *the chloride*, $CoCl_2.6H_2O$, and the *nitrate*, $Co(NO_3)_2.6H_2O$. The crude silicate, known as *smalt*, is largely employed in coloring glass and pottery deep blue.

Cobalt forms a large number of very complex compounds with ammonia which are known as cobalt amines. These combine with acids forming salts which are mostly highly colored. With a solution of potassium nitrite in presence of acetic acid cobalt salts form a beautiful crystalline yellow precipitate of potassium-cobalt nitrite, $K_3Co(NO_2)_6$.

The change of color on dehydration of a cobalt salt is shown in the next experiment. A common *sympathetic* ink is a dilute solution of the chloride or nitrate of cobalt, the use of which is here illustrated.

Experiment 175. Dip a clean pen into a dilute solution of cobalt chloride, $CoCl_2.6H_2O$, and write with it on white paper. When dry the writing is almost invisible. Now warm the paper

gently and carefully to avoid scorching it. Soon the writing becomes blue, and distinctly visible. If the paper is allowed to stand in the air some time the anhydrous salt, $CoCl_2$, absorbs moisture and returns to the almost colorless form.

Recognition. Cobalt compounds are recognized by the yellow nitrite precipitate just referred to and by forming a deep blue bead when fused with borax. This last behavior is extremely characteristic.

CHAPTER XXIV.

THE PLATINUM GROUP OF METALS: RUTHENIUM, RHODIUM, PALLADIUM, OSMIUM, IRIDIUM AND PLATINUM.

GENERAL CHARACTERISTICS.

These six metals are classed together in the eighth group or family of the Periodic arrangement, forming the last part of the fifth and eighth periods. The group of six naturally falls into two subgroups of three each, as the first three elements have atomic weights near 100 and the last three weights near 200. The proper scientific classification of these metals offers some difficulties because of the closeness in the atomic weights in each group, but for practical reasons they are always treated together.

The physical constants of the metals are shown in the following table:

	Atomic Weight.	Specific Gravity	Atomic Volume.	Melting Point.
Ruthenium	101.7	12.26	8.29	1800°
Rhodium	103.0	12.10	8.51	2000°
Palladium	106.5	11.8	9.00	1950°
Osmium	191.0	22.48	8.49	2500°
Iridium	193.0	22.42	8.61	2200°
Platinum	194.8	21.50	9.06	1775°

PLATINUM.

Occurrence. The six metals of the group are found associated in the ore known as *native platinum* which occurs in granular form in sandy or alluvial deposits in several parts of the world, more particularly in western Siberia. Smaller amounts are found in Australia, in

Mexico, in South America and in Borneo. Platinum is by far the most abundant of the metals in this ore, making up 75 per cent of it usually. The occurrence of platinum in other ores is quite unimportant.

History. This ore has been known in a general way since the middle of the eighteenth century, but it assumed no great importance until the English chemist Wollaston discovered a method of separating the platinum and bringing it into malleable condition. These discoveries were utilized by the London firm of Johnson, Matthey & Co., who, about 1810, began the manufacture of platinum articles for technical purposes. Many of the advances in the art of working the metal have been made by this firm.

Metallurgy. The ore is generally separated from the sands containing it by a systematic washing process, such as was referred to under gold. It is then worked up by one of two essentially different processes. The first of these is a modification of that originally devised by Wollaston and consists in dissolving out the metals by aqua regia, leaving sand and certain insoluble bodies behind. The strong solution of the chlorides, after evaporation to remove excess of acid, and dilution, is precipitated with an excess of ammonium chloride, which throws down the platinum in the form of a crystalline double salt, $(NH_4)_2PtCl_6$, with a small amount of the analogous iridium salt. The mother liquor contains nearly the whole of the other metals and a little of the platinum. All these may be precipitated in spongy form by metallic iron. The precipitate so obtained is heated with hydrochloric acid to free from traces of iron, dissolved in aqua regia and then reprecipitated by an excess of ammonium chloride as before. The resulting mother liquor is used for the preparation of the rarer elements, while the mixed platinum iridium precipitates are washed and converted into metal. This is done by heat, as the double salts are easily decomposed, leaving a spongy mass, which may be brought into compact form by hammering or, commonly, by fusing with the oxyhydrogen blowpipe in a

massive stone crucible. The metal obtained is not pure platinum but an alloy containing a little iridium, which for most purposes is practically better than the pure metal. The manufacture of pure platinum is an operation of considerable difficulty and will not be described here.

By another process, devised by Deville, in France, platinum is separated from the ore by a fusion method. The separation is effected by smelting with lead sulphide which combines readily with platinum and takes up but little of the osmium and iridium. The regulus of lead and platinum obtained is cupelled for separation of the lead by oxidation. The resulting platinum is sometimes pure enough for use directly but usually is subjected to further refining operations.

At the present time the total production of platinum is probably below about 10,000 pounds annually, and comes chiefly from Ural ores. The price of the metal is constantly advancing with the increased uses in the arts.

Properties. Platinum is very ductile and malleable, is a good conductor of heat and electricity and does not oxidize at any temperature. It does not dissolve in hydrochloric or nitric acid, but in a mixture of the two, or in liquids which liberate chlorine. When alloyed with silver small amounts are soluble in nitric acid. At a high temperature platinum is attacked by fused alkalies and phosphorus, also by many metals and heavy metallic salts. There is, therefore, a limit to the number of substances which may be heated or fused in platinum vessels. It alloys easily with many of the heavy metals.

By several methods platinum may be brought into a finely divided form known as platinum black or platinum sponge, and in this condition it absorbs gases readily. Several applications are made of this property in the arts.

Uses. Platinum is largely used in the manufacture of laboratory ware for a great variety of purposes, also in the construction of large stills for the distillation of sulphuric acid or for its concentration without distillation.

These large platinum vessels are rendered more durable by being plated with gold. Until 1845 the metal was used for coinage in Russia.

Platinum-Iridium alloys have come into use for the production of several articles. Much time has been spent in devising methods of separating both metals in perfectly pure condition, and alloys may now be obtained containing them in any desired proportion. A combination of 90 parts of platinum with 10 parts of iridium is very hard and withstands a high temperature. Because of these and other important properties it is used in the manufacture of the standard weights and measures in Great Britain. An alloy with 15 parts of iridium is used in making standard rules. Most of our laboratory platinum ware contains iridium.

Compounds of Platinum. Many of these are known, but few have any practical applications. Platinous chloride, $PtCl_2$, is known and a combination of this with potassium chloride, K_2PtCl_4, is employed in photography under the name of potassium chloroplatinite to give the dark or black effects in the toning of prints. The most important salt of platinum is the tetrachloride, $PtCl_4$, which is obtained by solution of the metal in aqua regia. It is used in chemical analysis for the separation of potassium, because under certain conditions it forms the insoluble compound K_2PtCl_6. The corresponding ammonium salt has been referred to above, as made in the process of separating platinum from its ore.

Recognition. The metal is usually recognized by the formation of these yellow precipitates.

The Other Platinum Metals.

Nothing more than brief mention need be made of these. *Iridium* is chiefly interesting and important because of the alloys it forms with platinum. To secure hardness the points of gold pens are often made of this metal. *Osmium* is always found in platinum ores and also in an ore with iridium alone. It has been obtained in

compact form and is the heaviest metal known. It forms a number of oxides, two of which have acid properties. Osmic tetroxide, OsO_4, or perosmic acid, is a volatile substance which is intensely poisonous, and which is used as a stain in microscopic work. *Ruthenium* and *rhodium* compounds have no practical applications. *Palladium* is interesting and important because of its property of absorbing large quantities of hydrogen, of which it will take up several hundred volumes under certain conditions. This property is applied in the analysis of gases containing hydrogen. By some chemists the product is considered as an *alloy* of palladium and hydrogen; others conclude that a *compound* of the formula PdH or Pd_2H_2 may be formed, and finally it may be looked upon as merely a mechanical mixture.

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